THE ROLE OF DONOR-ACCEPTOR COMPLEXES IN POLYMERIZATIONS INVOLVING 2,4,6-TRINITROSTYRENE

By

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1977

Dedicated to

Dr. G. B. Butler

For whose patience and encouragement

This modest work will be a standing testimony.

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to Dr. G.B. Butler for his stimulating guidance and for making my experience in research a rewarding one. I am also grateful to my supervisory committee for their comments and to Dr. T.E. Hogen-Esch in particular for the several useful discussions I had with him. I wish to extend my thanks to Dr. J.C.M. Tsibris for his permission to use the equipment in his laboratory for conductance and ESR studies.

My special thanks go to my parents and brothers without whose support and understanding this would not have been possible.

The memories I shall cherish of my colleagues will always be warm and pleasant for their mitigation of the frustrations of failure and for providing an extremely relaxed and cheerful atmosphere to work in. Among those I should mention especially are Drs. R.L. Veazey and A. Zampini to whom I owe much of my laboratory techniques. Discussions with Dr. C.F. Tien were quite valuable. I would also like to thank Ms. Carol Albert for her expert typing of the thesis.

Finally, I wish to acknowledge the warmth and affection of David and Esther Lane who lead my list of "unforgettable characters."

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Abstract of Dissertation Presented to the Graduate Council of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

The Role of Donor-Acceptor Complexes in Polymerizations Involving 2,4,6-Trinitrostyrene

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June 1977

Chairman: Dr. George B. Butler
Major Department: Chemistry

2,4,6-Trinitrostyrene (TNS) can be expected to behave as a powerful electron-acceptor because of the strong -I and -R effects of the nitro groups. TNS had been reported to undergo spontaneous copolymerization with electron-donor monomers such as 4-vinylpyridine (VP) and 4-(N,N-dimethylamino)styrene (DMAS). The initiation and propagation steps were believed to involve the donor-acceptor (D-A) complex for the following reasons: (1) TNS was not polymerizable, (2) the polymerizations were spontaneous, and (3) alternating copolymers were formed. The present work is a detailed examination of these reasons and of the role of the D-A complex in the polymerizations.

TNS was polymerized by initiating with tert-amines such as triethylamine, tributylamine and pyridine. Some of the other initiators used were: tributylphosphine, triphenylphosphine, NaCN/DMF and sodium tert-butoxide. N,N-dimethylaniline and N,N-dimethylamino-p-toluene were not capable of polymerizing TNS. The number average

molecular weight of the polymer was about 800. Polar solvents favored the polymerization indicating its ionic nature. Reducing the concentration of the initiator led to a decrease in conversion but no increase in the molecular weight. Polymerization at -17°C decreased the conversion and increased the molecular weight appreciably. These results were interpreted in terms of a high-energy propagation step. The initiation was postulated to be due to the nucleophilic attack by the amine on the double bond in TNS and not due to the D-A complex. Evidence for the former alternative was found by the reaction of diethylamine and pyridine with TNS and by the isolation of the intermediate products. Lack of conductivity and absence of ESR signals in the case of pyridine-TNS-DMSO systems was interpreted to be due to the insignificant "charge-transfer" in the complexes formed. Qualitative correlation between the nucleophilicities of the initiators and their initiating abilities was obtained.

The copolymerization of VP and TNS was also found to be favored by polar solvents. By analogy with the polymerization of TNS with pyridine, the nucleophilic attack by the pyridyl moiety on TNS was proposed to be the initiation step. The model compound for the 1:1 alternating copolymer of VP and TNS was synthesized and its spectra were compared with those of the copolymer. Evidence for the presence of both quaternized and

unquaternized pyridine rings was obtained from the PMR spectra. The former was believed to result from the initiation step and the latter, from the propagation step involving the D-A complex. The VP content of the copolymer was found to increase with increasing VP/TNS ratio in the monomer feed. It was also found that long reaction times led to cross-polymerization of the vinyl groups of the pyridinium rings at the end of each polymer chain formed initially by the random copolymerization of TNS and the VP-TNS complex.

DMAS gave polymers with 5% TNS and 5% trinitrobenzene. These polymers did not contain any TNS or TNB groups as shown by the ir spectra and elemental analyses. This was used as an evidence for the initiation by the D-A complex in the copolymerization of DMAS and TNS. Copolymerization attempts with N-vinyl carbazole (NVC) yielded only poly NVC. 2-Vinylnaphthalene and 3,5-dimethoxystyrene did not give any polymers. These results were interpreted in terms of geometric factors and low equilibrium constant respectively.

CHAPTER I
INTRODUCTION

General Background

The term "Donor-Acceptor Complex" usually denotes a large variety of combinations of molecules and ions, with Lewis acid-Lewis base interactions at one extreme and the various kinds of ion pairs at the other. For the purposes of this work, this will be taken to mean substances formed with localized interactions between the filled orbitals of the donor and the unfilled orbitals of the acceptor. This type of interaction falls between van der Waal's forces and the Lewis acid-base interactions and was first studied by Mulliken. Mulliken proposed that the bonding between a donor (D) and an acceptor (A) might be described as a combination of a "no bond" wave function [$\Psi_{1(A,D)}$] and a "dative" wave function [$\Psi_{2(A^-,D^+)}$].[1] This is represented in Equation 1.

$$\Psi_N = a\Psi_{1(A,D)} + b\Psi_{2(A^-,D^+)} \qquad \text{Eq. 1}$$

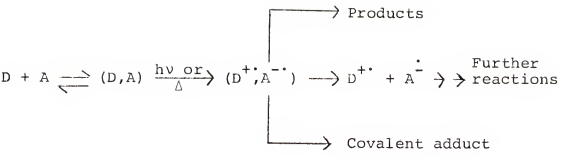
The stabilization of such complexes is then attributed to the contribution from the ionic structure as represented by the second terms in Eq. 1. Accordingly, Mulliken called these complexes "charge-transfer" complexes. The extent

of contribution by the "charge-transfer' structure will depend on the ionization potential of the donor and the electron affinity of the acceptor. For most complexes, however, b>>a in the excited state and a>>b in the ground state.

The chemical reactivity of the complex will be determined by factors such as the geometry of the complex, stabilization of the positive charge on the donor and of the negative charge on the acceptor, etc. The complex may participate in chemical reactions either as one single cohesive unit or simply as a promoter or inhibitor of the reactivity of one component. A critical assessment of the possibilities for the involvement of donor-acceptor complexes in organic reactions has been made by Kosower.[2] In polymerization reactions, the complex may be expected to play the roles of both initiator and propagator. A comprehensive review of this dual role has been made by Hyde and Ledwith.[3]

D-A Complexes as Initiators

Reactive intermediates can be produced from D-A complexes by thermal and photochemical means and the products may initiate polymerization. This is summarized in Scheme 1. It is conceivable, at least in principle, that complex formation can ultimately lead to the simultaneous production of an anion, a cation and radicals. Initiation by the complex can then possibly lead to both ionic and radical polymerizations. The nature of



Scheme 1

the actual process will, of course, be dictated by the monomers, solvent, temperature, etc. An example of how reaction conditions may alter the course of such polymerizations is provided by the work of Tada, et al. on the polymerization of N-vinyl carbazole (NVC) in the presence of electron-acceptors like chloranil and 1,3,5-trinitrobenzene.[4] Photolysis of the system at the charge-transfer band in less basic solvents like methylene chloride led to the formation of poly-NVC through a cationic mechanism, whereas in basic solvents like DMSO, it proceeded through a radical mechanism. An unusual thermal initiation is reported by Stille, et al. in the copolymerization of ethyl vinyl ether (EVE) and vinylidene cyanide (VCN).[5] On mixing at room temperature, copolymers were formed along with poly-EVE and poly-VCN. Since poly-EVE can be formed only through a cationic mechanism and poly-VCN, only through an anionic mechanism, the donor-acceptor complex was proposed to be the initiator of all polymerizations.

D-A Complexes in the Propagation Step

While the involvement of D-A complexes in the initiation step has been clearly demonstrated, their participation in the propagation step has been shown unequivocally only in very few systems. The difficulty arises due to the fact that conventional tools like solvent effects have to be used with great reservation. It is now recognized that the monomer-solvent interaction is of great importance in complex formation.[6] The complex formation also shows high temperature sensitivity.[7] These considerations make choice of reaction conditions very narrow and interpretation of results very difficult. Generally, formation of copolymers with a high degree of alternation has been taken to imply polymerization through a complex. The shortcoming of this method is that the alternation may simply be fortuitous as in the case of styrene and methyl methacrylate. However, alternation over a broad range of monomer feed-ratios may be considered to be in support of this proposal. It has also been frequently assumed that the complex will be so highly reactive as to make competition from the free monomers negligible. Recent work has shown that addition of free monomers to the growing polymer chain may be important and had been underestimated.[8] Perhaps a more valid method to test the hypothesis is to study the rates of polymerization at different monomer feed ratios. This method rests on the reasonable assumption that the rate of polymerization will be greatest when the complex

concentration is largest, i.e. at the monomer feed-ratio corresponding to the stoichiometry of the complex. It proved useful in the case of the NVC-fumaronitrile system.[9] Several authors have derived kinetic equations but their applicability has been limited because of the assumptions made in their derivations.[10] Another frequent source of ambiguity is the structure of the polymerizing complex. It is not clear whether it is in the ground state or in the excited, ionic state as assumed in several systems.[11]

One of the most extensively studied systems is that of styrene and maleic anhydride. Styrene acts as a donor and forms alternating copolymers over a wide range of reaction conditions. The copolymerization was faster than the homopolymerization of styrene which was attributed to the increased reactivity of the complex. Solvent effects also pointed to the same conclusion. Similar behavior has led Butler and Campus to conclude that the complex may compete quite effectively with the free monomers in the copolymerization of vinyl silanes and divinyl ether with maleic anhydride.[12] Picryl methacrylate did not undergo radical polymerization but, under identical conditions, copolymerized with 2-naphthyl-methacrylate. The copolymer composition depended on the amount of solvent present and this was used as an argument in favor of participation by the complex.[13]

Copolymerization of 2,4,6-Trinitrostyrene

Yang and Gaoni first reported the copolymerization of 2,4,6-trinitrostyrene (TNS) with 2- and 4-vinyl pyridines (VP) and N,N'-dimethylaminostyrene (DMAS).[14] The copolymerization occurred exothermically upon mixing the two monomers at room temperature. After the mixture was dissolved in pyridine and treated with ether, copolymers of molecular weight 6000-8000 were obtained in about 60% yield. The presence or absence of oxygen made no difference. The copolymers formed were somewhat soluble in chloroform, acetone and DMF but insoluble in ether and aliphatic hydrocarbons. 4-VP formed copolymers with 50% and 67% composition, depending on the feed ratio. 2-VP gave a copolymer with 1:1 ratio while the DMAS-TNS copolymer had the composition 2:1.

The structures of the copolymers were determined from their UV spectra. The copolymers displayed two unusual properties: (1) These copolymers exhibited strong and broad charge-transfer transitions near 450 nm which obeyed Beer's Law, and (2) the extinction coefficients of the C-T transitions were anomalously high. The C-T interactions in the copolymers were not perturbed by the solvent environment and showed no visible dissociation over a concentration range of 5×10^{-4} to 1×10^{-6} M in acetone or DMF. This phenomenon was rationalized by the explanation that the donating and accepting groups in the copolymer were held together by the polymer network and

thus were unaffected by the solvent. The intensification of the C-T transitions was proposed to be due to the coupling of adjacent donor-acceptor oscillators, i.e., due to the delocalization of an excited donor-acceptor couple to the adjacent D-A couple as shown in Equation 2.

$$+\text{D-A-D-A-D-A}+ \xrightarrow{h\nu} +\text{D-A-D}^{+}\text{A}^{-}\text{-D-A}+ \longleftrightarrow +\text{D}^{+}\text{A}^{-}\text{-D-A-D-A}+$$

Eq. 2

From these observations, the authors proposed an alternating structure for the copolymers formed.

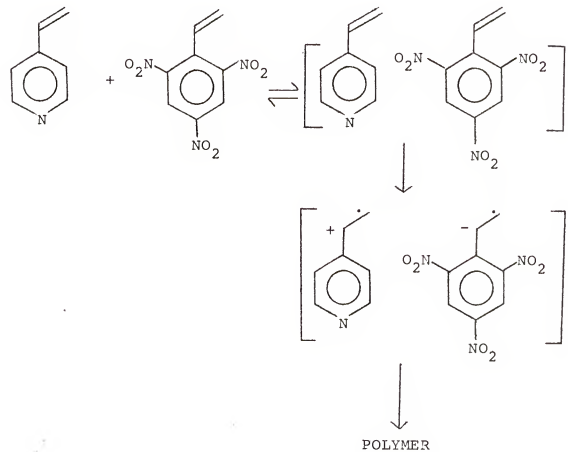
Mechanism of Copolymerization

Based on the above results, Yang and Gaoni concluded that the D-A complex was involved both in the initiation and propagation steps. Their arguments in favor of such a scheme may be summarized as follows:

(1) TNS was not homopolymerizable. If this were true, segments like -TNS-TNS- could not be present in the copolymer. Hence, any TNS present in the copolymer must have come through the complex participating in the propagation step.

(2) The copolymerization proceeded spontaneously without any added initiators. This spontaneity was presumably due to the D-A complex acting as initiator. Taking these two aspects together, Yang and Gaoni concluded that "sufficient delocalization of the complex

occurred to initiate and propagate in the polymerization." Subsequently, it has generally been assumed in the literature that the polymerization may be envisioned as follows:

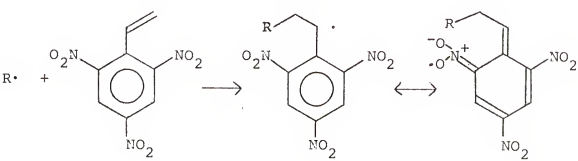


Scheme 2

(3) The strongest evidence in favor of Scheme 2, according to the authors, was the formation of 1:1 alternating copolymers.

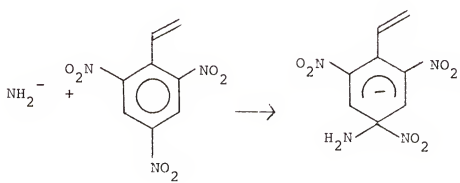
The Problem and Methodology of Investigation

The failure of early attempts to polymerize TNS was most likely due to poor choice of conditions. For example, Wiley and Behr tried to polymerize TNS with benzoyl-peroxide.[15] Nitro groups, being excellent quenchers for radicals, inhibited the radical "polymerizations." There is also another important factor viz. the proximity of the incipient radical site in the vinyl group to the nitro group in the aromatic ring. This situation is represented in the following equation.



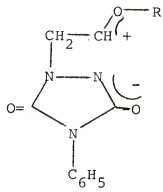
This quenching was, not surprisingly, strong enough to inhibit the polymerization completely. Similarly, the ineffectiveness of NH_2^- to initiate the polymerization of TNS[16] can be attributed to the highly stable σ-complex formation by the anion with the aromatic ring. Structures like Eq. 4 are possible and these, once formed, can effectively stop any polymerization because of reduced reactivity. Similar complexes with CH_3O^- are well-known and have been characterized.[17] One of the objectives of

this project will be to make the proper choice of initiators and investigate fully the polymerizability of TNS.



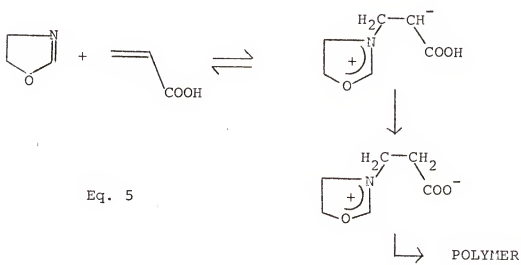
Eq. 4

The spontaneous nature of the polymerization simply means that the initiator is formed from the monomer pair. Donor-acceptor complex is definitely a strong possibility. Several examples of initiation by such complexes are now available. There is a report that p-amino styrene polymerized at room temperature in dichloromethane in the presence of electron-acceptors like chloranil and trinitrobenzene.[18] That should not preclude, however, consideration of other mechanistic possibilities. There are several cases of donor-acceptor systems where the spontaneous polymerization is due to a dipole or zwitterion. An example is the copolymerization of divinyl ether (DVE) and 4-phenyl-1,2,4-triazoline-3,5-dione (PhTD).[19] PhTD is a very powerful acceptor and DVE is a donor. The formation of a dipole such as shown in Structure I is now clearly established.



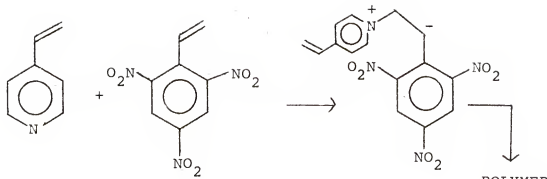
I

Another well-characterized system is that of oxazoline (donor) and acrylic acid (acceptor). From the exhaustive data of Saegusa's group, the copolymerization is now recognized to proceed through Zwitterions of the type in Equation 5.[20]

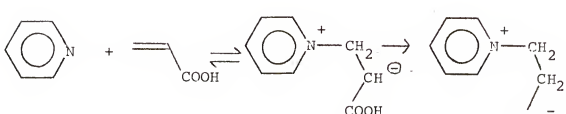


Eq. 5

This alternative will be considered in this work and may be represented as in Scheme 3. Nucleophilic attack by the nitrogen in pyridine is known in at least one other case as in Equation 6.[21]



Scheme 3

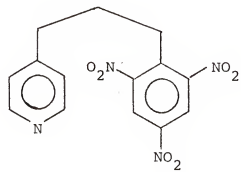


Eq. 6

In the case of TNS, the negative charge will be highly delocalized over the ring and the nitro groups and should be very stable.

The evidence for the alternating structure of the VP-TNS copolymer is, at best, insufficient. Another important aspect of this project will be to determine the micro structure of the copolymer by PMR and ^{13}C nmr. Model compounds and homopolymers of VP and TNS may be used for comparative purposes. Synthesis of 4[3-(2,4,6-trinitro)phenyl propyl]-pyridine (Structure II), a model compound for the 1:1 alternating copolymer, will be

attempted. Comparison of other polymerization systems involving powerful donors like 2-vinyl naphthalene, N-vinyl carbazole and 3,5-dimethoxystyrene will also be undertaken to estimate the role played by the D-A complex in these copolymerizations.



II

CHAPTER 2
OLIGOMERIZATION OF TRINITROSTYRENE

Previous Attempts to Polymerize Trinitrostyrene

The synthesis of 2,4,6-trinitrostyrene (TNS) was first reported by Wiley and Behr.[15] As a monomer, TNS can be expected to be a very strong acceptor due to the powerful -I and -R effects of the nitro groups. In fact, these effects are so pronounced as to make the vinyl group electrophilic in character. Illustrative of this is the failure of bromine to add to the double bond.[16] It has now been established that in the bromine addition to double bonds, the initial attack is by the electrophilic bromonium ion. Again, the addition of NH_3 to TNS to give the corresponding substituted amine is indicative of the electron-deficiency of the vinyl group.[16]

A variety of initiators had been tried for the homopolymerization of TNS. Wiley and Behr[15] used benzoyl peroxide but reported no polymerization up to a week. TNS also failed to copolymerize with styrene under similar conditions. BF_3 had been used as an initiator for the polymerization of 4-nitrostyrene but was found ineffective in the case of TNS.[15] The inability of radical initiators can be attributed to the inhibiting action of the nitro groups. As part of this work, several anionic initiators were tried. Strong ionic bases like

n-butyl lithium and sodium methoxide failed as did sodamide. This is perhaps due to some interaction between the nitro groups and the ionic bases. It is well-known, for example, that Wittig reactions become increasingly difficult with increasing number of nitro groups.

Polymerization of TNS with Amines

It is reasonably clear that for an initiator to be successful in effecting the polymerization of TNS, it has to be nucleophilic but not extremely basic. Amines fit these requirements excellently and several of them were found to be successful in initiating the polymerization of TNS. There is at least one report of amines being able to initiate polymerization of nitro monomers viz. nitroethylene.[22] A comparative list of the effectiveness of several compounds in initiating the polymerization of TNS is given in Table 1.

The polymer so obtained was a brownish powder which was subsequently purified by repeated extractions with ether and chloroform to remove unreacted monomers. It was soluble in acetone, DMSO, and DMF but insoluble in ether, benzene and aliphatic hydrocarbons. The number-average molecular weight as determined by Vapor Pressure Osmometry was 797, corresponding to a degree of polymerization of 3.3.

Several factors may be responsible for the unusually low molecular weight. The simplest reason could be a

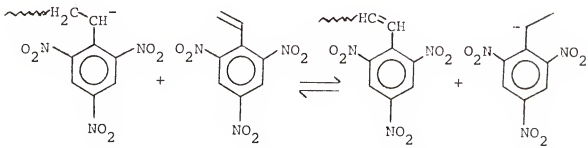
Table 1

Effectiveness of Compounds as Initiators for the Polymerization of TNS

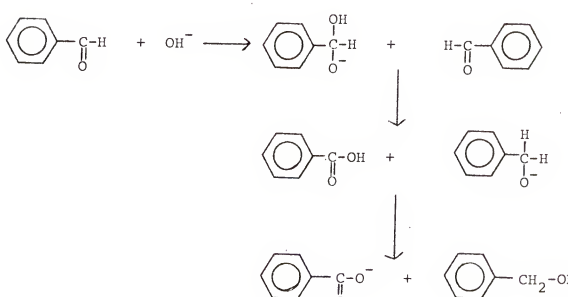
Initiator	Concentration[a]	Whether effective	Ref.
Benzoyl peroxide	0.1%	No	15
BF_3/C_2H_5Cl	Saturated solution	No	15
$(NH_4)_2S_2O_8/NaHSO_3$	--	No	15
$NaNH_2$	--	No	16
n-Butyl lithium	--	No	This work
$NaOCH_3$	--	No	This work
NaO-t-C_4H_9	--	Yes	This work
NaCN/DMF	Saturated solution	Yes	This work
$(C_2H_5)_3N$	2.5%, 5%, 10%	Yes	This work
$(n\text{-}C_4H_9)_3N$	5%, 10%	Yes	This work
Pyridine	5%, 10%	Yes	This work
N,N-Dimethylaniline	10%, 50%, excess	No	This work
N,N,4-Trimethylaniline	10%, 50%, excess	No	This work
N,N,N',N'-Tetramethyl-hexane diamine	5%	Yes	This work
Triphenyl phosphine	5%, 10%, 30%	Polymerization at high concentration	This work
Tri-n-butyl phosphine	5%, 10%, 30%	Polymerization at high concentration	This work

[a]Concentrations of initiators are given in mole percent of the TNS.

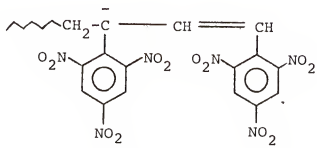
propagation step of high activation energy which would mean slow growth of the polymer chain and low kinetic chain length. Steric factors may determine the height of this energy barrier. A second plausible reason is chain transfer, especially to the monomer as shown below:



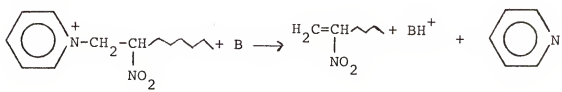
Intermolecular hydride transfers like these have been shown to occur in anions. Cannizzaro's reaction, involving aldehydes without α-protons and hydroxide ions, takes place through a hydride shift.



Intramolecular abstraction of the proton α- to the phenyl ring is also possible, especially at the chain-end to give rise to structures such as



Regeneration of the initiator can also bring about low molecular weight as in the polymerization of nitroethylene initiated by pyridine.[22]



Solvent Effects

The solvent effect on the polymerization initiated by triethylamine is summarized in Table 2. Polar solvents favor the polymerization, thus indicating the ionic (most likely anionic) nature of the initiating and/or propagating steps.

With the view to prepare polymers of higher molecular weight, two different reaction conditions were tried. They were:

(1) Varying concentrations of the amine initiator, and

(2) Polymerization at low temperature in a suitable solvent.

Table 2

Polymerization of TNS in Different Solvents

Solvent	Dielectric Constant	Polymer Yield[a] in g	% Conversion
Dioxane	2.209	0.011	2.2
THF	7.58	0.090	18.0
1,2-Dichloroethane	10.36	0.189	37.8
Acetonitrile	38.8	0.266	53.2
DMSO	46.68	0.334	66.8
DMSO-H_2O[b]	--	0.287	57.4

[a] Reaction conditions: [TNS] = 2.09 M, [Et_3N] = 10%, at room temperature for 24 hrs.

[b] DMSO:H_2O::9:1 (By weight).

Dependence on the Concentration of the Initiator

The first approach was taken because it is generally true in radical and anionic polymerizations that the molecular weight varies inversely with the number of growing chains which in turn, is directly related to the initiator concentration. The relationship between the number average degree of polymerization ($\overline{X}_n$), kinetic chain length (ν) and the initiator concentration ([I]) for a polymerization initiated by the thermal homolysis of an initiator is given by,

$$\overline{X}_n \propto \nu = \frac{k_p[M]}{2(fk_dk_t[I])^{1/2}}$$

where k_p = rate constant for propagation,

k_t = rate constant for termination,

k_d = rate constant for the thermal decomposition of the initiator

and f = initiator efficiency.

In anionic polymerization where all of the initiator is converted to propagating polymer chain-ends, the number-average degree of polymerization is,

$$\overline{X}_n = \frac{[M]}{[I]}$$

The results are given in Table 3. Two significant but apparently conflicting trends are immediately obvious. Firstly, the conversion decreases with decreasing concen-

Table 3

Effect of Initiator Concentration on the Polymerization of TNS

Concentration of $(C_2H_5)_3N$[a]	Conversion	Molecular Weight[b]
10%	70.4%	797
5%	50%	---
2.5%	20%	833

[a]Initiator concentration is expressed as mole percent of the TNS.

[b]Determined by Vapor Pressure Osmometry.
Reaction conditions: [TNS] = 3 M, Solvent: DMSO, Reaction time: 69 hrs at room temperature.

tration of the initiator. This is to be expected because decreasing the concentration of the initiator will lead to a reduction in the number of the initiating species. The molecular weight, however, does not increase significantly. This is possible if, for some reason, the propagation step is sluggish. Such may be the case in this system where great steric factors may play an important role.

There is reason to believe that the nitro groups ortho to the vinyl group in TNS exert considerable steric strain on the whole molecule. In 2,4,6-trinitrochlorobenzene which is similar to TNS the nitro groups at the 2- and 6-positions are twisted and are almost perpendicular to the plane of the aromatic ring.[23] The situation may well be so in TNS and in the oligomer being formed. It is conceivable that the bulky trinitrophenyl groups discourage further addition of monomer after a certain degree of polymerization. Space filling models do indeed show a very large amount of steric crowding and perhaps the growing polymer chain-end is deeply buried among the pendant trinitrophenyl groups. This will lead to decreased reactivity of the growing chain-end. Another important factor that may also contribute to the reduced reactivity is the stability of the carbonion that may be formed (See below). The reactivity of a chemical species depends on its stability, with the more stable ones showing less reactivity and vice versa.

Polymerization at Low Temperature

The second approach, namely the effect of temperature on the polymerization, was studied by carrying it out at -17°C in acetonitrile again with triethylamine as the initiator. The activation energy for the degree of polymerization in cationic and anionic polymerizations is ($E_{propagation}$ - $E_{termination}$). For most ionic polymerizations, this term is negative because the activation energy for termination is usually greater than the activation energy for propagation. For example, this difference is -4 Kcal/mole for the potassium amide polymerization of styrene. Thus, a decrease in the temperature of polymerization is followed by an increase in the degree of polymerization. The activation energy for the overall polymerization is ($E_{initiation}$ + $E_{propagation}$ - $E_{termination}$) and has usually a positive value. This is to be expected because in the initiation step of most ionic polymerizations, species of opposite charge are separated and this requires very high energy. Some of this energy requirement may be met by the partial solvation by the solvent, especially at low temperature but frequently the overall term remains positive. Consequently the rate of polymerization decreases as the temperature decreases. A comparison of the polymerizations at room temperature at at -17°C is given in Table 4.

The % conversion, which is a measure of the rate of polymerization, decreases as the temperature decreases but the molecular weight shows a relatively significant

Table 4

Effect of Temperature on the Polymerization of TNS

Temperature	Conversion	Molecular Weight
Room temp (25°C)	34%	736
-17°C	13%	1080

Reaction conditions: [TNS] = 3 M, [Et_3N] = 4.8%, Solvent: CH_3CN; Reaction Time: 64.5 hrs. Molecular weight by VPO.

increase. These two trends fit with the explanations above for ionic polymerizations, confirming once again the nature of polymerization of TNS. The drop in conversion suggests a significant decrease in the number of propagating species. This could have resulted either from a decrease in the number of initiating species or from a terminating step of high activation energy or a combination of both. It is highly unlikely that the former is the reason because formation of Zwitterions (see below) show little or no temperature effect. If it does at all, it is perhaps reasonable to predict that low temperature will favor the formation of ionic species due to increased solvation. This leaves us with the alternative explanation of a slow propagation step and a termination step of high activation energy. The effect of initiator concentration on the molecular weight also reinforces this conclusion. The increase in molecular weight at -17°C, though significant, is not large in absolute terms. This is probably a reflection on the small difference between

$E_{propagation}$ and $E_{termination}$.

Possible Mechanisms

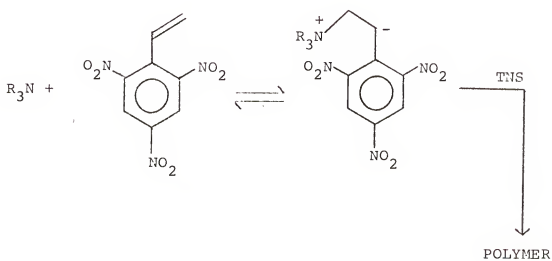
Consistent with all these features, at least two mechanisms can be proposed for the initiation of the polymerization of TNS. They are:

(1) The donor-acceptor complex mechanism (Scheme 4) and

(2) The Zwitterion mechanism (Scheme 5).

$$TNS + Amine \rightleftharpoons [TNS, Amine] \rightleftharpoons [TNS^{\dot{-}}, Amine^{\dot{+}}] \rightleftharpoons Amine^{\dot{+}} + TNS^{\dot{-}} \xrightarrow{TNS} Polymer$$

Scheme 4



Scheme 5

In Scheme 4, the amine initiator and the TNS form a donor-acceptor complex followed by charge transfer from the donor to the acceptor. The resulting species, either the ion pair or free ion(s), is responsible for the initiation of polymerization. The critical step is the one involving transfer of charge which enhances the ionic character of the complex. Similar mechanisms have been invoked to explain the polymerizations of alkyl vinyl ethers and N-vinylcarbazole in the presence of electron-acceptors.

In Scheme 5, the initiation is due to a Zwitterion formed by the nucleophilic attack of the amine on the double bond in TNS. The propagating step will then be subsequent addition of monomers to the negative end of the dipole. There are numerous examples of Zwitterions as the initiating and propagating species in polymerizations.

Comparison of the Mechanisms

It is possible to compare the two schemes in detail and list some of their implications as follows:

(1) In Scheme 4, the donor-acceptor complex between the amine and TNS is given a large ionic character by the partial or complete transfer of charge from the donor to the acceptor. This charge-transfer will depend on the nature of the donor, solvent, electron-affinity of the acceptor, etc. The ion pair which may be formed initially will be expected to dissociate into free radical ions in

solvents of high dielectric constant, like DMSO. The production of free ions will be accompanied by an increase in the conductivity of the system. This is conceivable only when the radical ions are sufficiently stable and not very reactive. There is reason to believe that this is indeed the case in similar systems. Miller and Wynne-Jones observed an increase in conductivity during the complex formation between 1,3,5-trinitrobenzene and aliphatic amines.[24] The Zwitterion formed in Scheme 5, on the other hand, should show little or no increase in conductivity at least in the early stages of the reaction.

(2) If initiation is indeed due to the ion pair or free ions as in Scheme 4, the ionization potential of the donor should play a large role in the initiation step. As a first approximation, it is reasonable to assume that the lower the ionization potential of the donor, the greater the possibility of charge-transfer and hence greater the efficiency of the donor-initiator. In contrast, Scheme 5, if operative, should show a dependence on the nucleophilicity of the initiator.

(3) The complete dissociation of the ion pair in polar solvents gives rise to radical ions. If these are in sufficient concentration, ESR spectra should prove useful in detecting their presence. An absence of ESR signals does not, however, prove unequivocally that Scheme 5 is operative but can be interpreted to be strongly against the donor-acceptor complex mechanism.

Conductance Studies

The conductivities of TNS in the presence of several amines in DMSO were measured at room temperature. The dielectric constant of DMSO being very high (ε:46.68), it is reasonable to assume that all ion pairs, if formed, will dissociate rapidly into free ions. Table 5 gives a summary of all the relevant data. For comparative purposes, similar measurements were made on some 2,4,6-trinitrotoluene-amine systems in DMSO. It is clear that the two systems show similar trends which suggests that any increase in conductivity is probably the result of some fundamental process like charge-transfer and not due to any secondary reactions that may possibly arise from the Zwitterions as proposed in Scheme 5.

It is quite evident from the data in Table 5 that the mixtures of TNS with DMA and pyridine do not show any significant increase in conductance thereby indicating that these complexes do not have appreciable ionic character even in DMSO. The dramatic 300-fold increase in the conductance of TNS on adding triethylamine suggests the formation of a large number of ionic species. This could have resulted from electron transfer in the complex. The relatively small increase in the case of tributyl amine can partially be explained by the difference in the mobilities of the corresponding ions, namely $(C_2H_5)N^+$ and $(C_4H_9)_3N^+$. The former should have a higher mobility than the latter because of its smaller size. Of course,

Table 5

Conductivities of DMSO Solutions of TNS and TNT in the Presence of Amines

Solution	TNS[1]		TNT[1]	
	[TNS]/[Amine]	Conductance $\mho$ ($\times 10^6$)	[TNT]/[Amine]	Conductance $\mho$ ($\times 10^6$)
TNT or TNS (X)	--	2.9	--	8.5
Et_3N	--	2.4	--	2.4
X + Et_3N	14	1.5×10^3	21	1.7×10^3
n-Bu_3N	--	1.6	--	
X + Bu_3N	14	98	--	
(N,N-Dimethylaniline) DMA	--	0.65	--	
X + DMA	14	8.7	--	
Pyridine	--	0.2	--	0.2
X + Pyridine	9.06	8.0	7.6	22

[1]Concentration was 1.25 M.

All measurements were made at room temperature. Conductance of DMSO: 0.6×10^{-6} $\mho$.

this assumes that the solvation of the two species is not very different. However, this may not be the entire picture as the ionization potential of tributyl amine is slightly (about 0.2 ev) less than that of triethyl amine. Perhaps the great increase in the case of triethyl amine is the result of some impurity like adventitous water. In any case, the relevant conclusion that can be made from Table 5 is that if pyridine acts as an initiator in the polymerization of TNS, there must be some factor other than the "charge transfer" complex.

Effectiveness of the Initiators

Table 6 compares the effectiveness of some amines as initiators in the polymerization of TNS with regard to their ionization potentials, pK_a and electron donating power ($\Delta\nu_D$). The ionization potentials were estimated from the charge-transfer spectra of the amines with acceptors like iodine or trinitrobenzene in non-polar solvents. This procedure is known to give values in agreement with other independent methods[25] for the determination of ionization potentials. The $\Delta\nu_D$ values were taken from the data of Kagiya, et al., who found that the ir absorption of the O-D band in CH_3OD varied in a regular fashion with a wide variety of electron donors.[26] They also found that this resulted from an interaction between the donor and the O-D bond. From the shifts in the ir absorption they were able to construct a scale of "nucleophilic solvation". The higher the $\Delta\nu_D$ value, the greater the shift and the more nucleophilic

Table 6

Comparison of Initiator Efficiency

Compound	Whether capable of initiation	Ionization potential, ev[a]	$\Delta\nu_{D}$ [b] cm^{-1}	pK_a [c]
Et_3N	Yes	7.50	238	10.78
$n\text{-}Bu_3N$	Yes			11.04
Pyridine	Yes	9.32	168	5.19
3-Chloropyridine	Only at high concentrations	9.33		2.84
N,N-Dimethylaniline	No	7.3	148	5.18
N,N-4-Trimethylaniline	No			5.61

[a] From "Organic charge-transfer Complexes" by R. Foster, Academic Press, 1969, p. 384; M.W. Hanna and J.L. Lippert, p. 38ff in "Molecular Complexes," Vol. 1 ed. by R. Foster, Crane, Russak & Co., 1973.

[b] T. Kagiya, Y. Sumida and T. Inoue, Bull. Chem. Soc., Japan, 41, 767 (1968).

[c] From "Dissociation Constants of Organic Bases in Aqueous Solutions," by D.D. Perrin, Butterworths, London, 1965.

the donor is. It is generally true that for similar compounds, the nucleophilicity values are in line with their pK_b or basicity values.[27] For this reason, a rather crude scale of nucleophilicity may be derived from a comparison of the pK_a or pK_b values. This type of correlation works best only when the nucleophiles being compared are very similar in structure as, for example, substituted pyridines, phenoxides, etc.

A close examination of the data in Table 6 reveals no correlation between the ionization potentials of the amines and their effectiveness as initiators. On the contrary, there seems to be some qualitative dependence on their nucleophilicity. This is borne out in a particularly marked fashion in the cases of pyridine and 3-chloropyridine. The former is a stronger base and a better initiator. It is important to realize that a basic assumption in this treatment is that altering the structures of the components has little effect on the complex formation. While this is not always true, the closeness in the ionization potential values for the two pyridines may be expected to give some validity to the assumption. The similar pK_a values for pyridine and N,N-dimethylanilines and their efficiencies as initiators only exemplify the limitations of interchanging the concepts of basicity and nucleophilicity. However, their $\Delta\nu_D$ values are different enough to account for their initiating abilities.

ESR Studies

The ESR spectra of TNS-triethylamine system in DMSO are shown in Figures 1 and 2. As soon as the components were mixed, there was a moderate signal with a g value of 2.004. The signal weakened rapidly with time and after about 10 minutes, it vanished completely. The exact structures of the radicals formed were not determined due to the lack of hyperfine splitting. In general, the hyperfine splitting improves with dilution of the sample to provide details of the structure of the radical. In this case, the signal decreased in intensity on dilution and seemed to be less stable. Variation of temperature was not tried. It is reasonable to assume that the concentration of the radicals was quite low. In any case, a more important and perhaps more relevant observation was that no such signals were detected in the case of TNS-pyridine and TNS-4-vinylpyridine in DMSO. Even when equimolar concentration was employed, the vinylpyridine-TNS system did not show any signal. This behavior would seem to point to the relatively small, if any, contribution of the 'dative' structure to the complexes of TNS with VP and pyridine. This conclusion also reinforces the earlier one based on the conductance measurements. It is also of interest to note that a similar situation was encountered with the TNT-triethylamine and TNT-pyridine systems. These spectra showed more structure but not enough to permit any detailed or even semi-quantitative analysis.

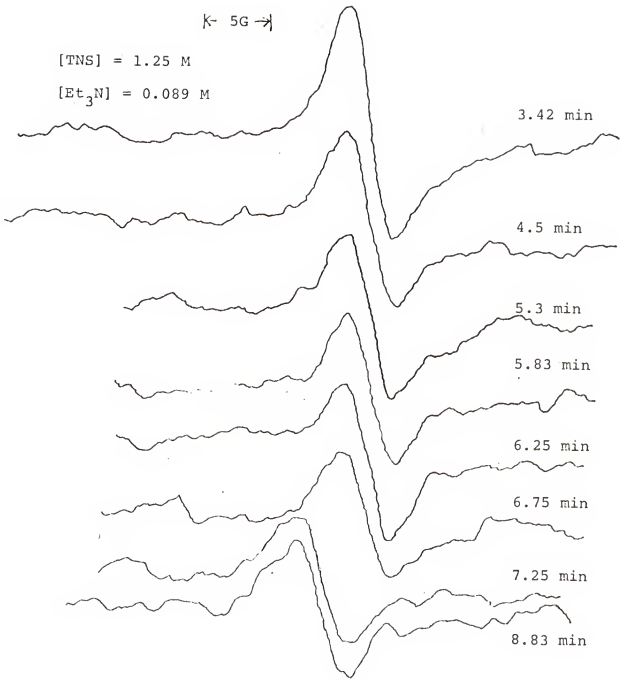


Figure 1: ESR Spectra of TNS and Et_3N in DMSO

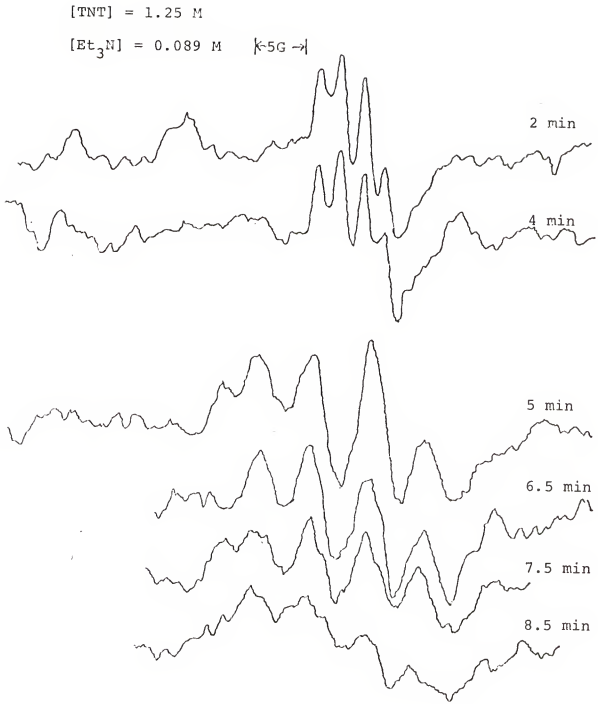
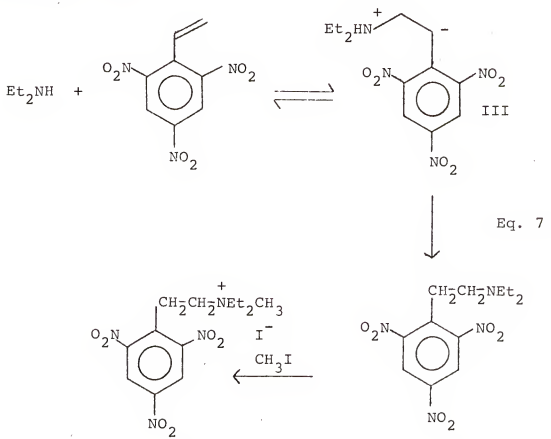


Figure 2: ESR Spectra of TNT and Et_3N in DMSO

Evidence in Favor of the Zwitterion Mechanism

A strong evidence in favor of the nucleophilic attack of the amine comes from the reaction of diethylamine with TNS in solvents like dioxane and acetonitrile as shown below.

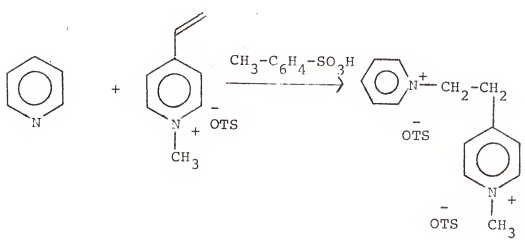


Solvent	Reaction time	Yield of the quaternary salt
Dioxane	24 hrs	52%
Acetonitrile	24 hrs	53%

The Zwitterion III is different from similar Zwitterions resulting from triethylamine in that the former can collapse by the transfer of a proton from the nitrogen

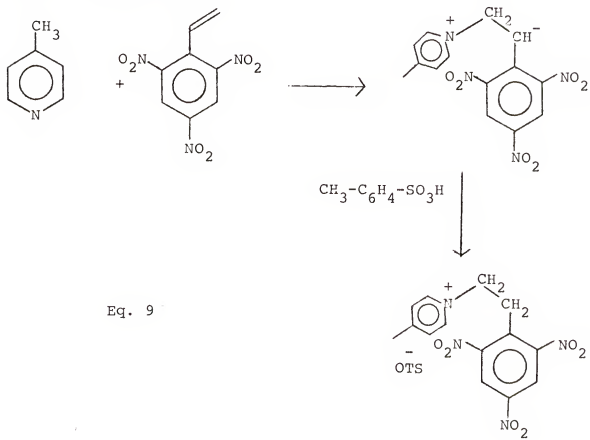
to the trinitrobenzyl anion. The solvent effect is also consistent with ionic intermediates. Qualitatively the reaction was faster in acetonitrile than in dioxane. The quaternary salt was synthesized independently from 2,4,6-trinitrotoluene, formaldehyde and diethylamine via a Mannich-type condensation. The two compounds showed identical physical properties. Similar reactions were tried with pyridine but no quaternary salts could be isolated. In this connection, it is interesting to note that isolation of TNT-pyridine complexes from solution have proved to be unsuccessful.[28]

The initial failure to isolate the pyridinium analog of structure III prompted a variety of reaction conditions. Salamone, et al., have prepared similar compounds by conducting the reaction with the pure pyridine derivative as the medium.[29] This is represented in Equation 8.



Eq. 8

It is conceivable that TNS can also react in a similar manner to give the corresponding quaternary salt. This turned out to be the case when TNS was mixed with excess 4-picoline and p-toluene sulfonic acid. The reaction is shown in Equation 9.



Eq. 9

Equations 7 and 9 conclusively prove that the initiation of the polymerization of TNS is indeed due to the nucleophilic attack by the amine on the double bond.

CHAPTER 3
COPOLYMERIZATIONS OF TNS

Complexes of 2,4,6-Trinitrotoluene (TNT)

With the idea of preparing copolymers of TNS using the concept of donor-acceptor complexes, several donor monomers were tried. These were 4-vinylpyridine (VP), N,N'-dimethylaminostyrene (DMAS), N-vinylcarbazole (NVC), 2-vinylnaphthalene (VN) and 3,5-dimethoxystyrene (DMS). All of them formed complexes with TNS as evidenced by the dramatic color changes brought about when one was added to the other in solution. To estimate the relative strengths of these complexes, a comparison of the equilibrium constants of the methyl analogs was made. The K values which were measured using UV and nmr spectroscopy and the Benesi-Hildebrand equation are listed in Table 7.

In extrapolating the equilibrium constants of the model compounds to the strengths of complex formation of the monomers themselves, it should be noted that the former can only set a lower limit for the latter. For example, consider the equilibrium constants for the iodine complexes of toluene and styrene in carbontetrachloride. The K value for the former is 1.65 l mole^{-1} while that for the latter is 3.2 l mole^{-1}.[30] The increase

Table 7

Formation Constants for the Complexes of TNT with Donors at Room Temperature

Donor	Equilibrium Constant	Method	Reference
4-Picoline	0.13 l^2 $mole^{-2}$	UV	Yang & Gaoni
N,N'-Dimethyl p-toluidine	0.60 l $mole^{-1}$	UV	Yang & Gaoni
3,5-Dimethoxy-toluene	0.11 l $mole^{-1}$	NMR	This work
N-Ethylcarbazole	0.72 l $mole^{-1}$	UV	This work
2-Methylnaphthalene	0.99 l $mole^{-1}$	UV	This work

Solvent: CH_2Cl_2

in the association constant for styrene is probably the result of the increased overlap between the two species facilitated by the π orbitals of the vinyl group. The following sections describe each monomer system at length.

With Vinylpyridine

4-Vinylpyridine, a clear, colorless liquid, turned purplish red on adding the bright yellow TNS. The mixture became viscous after about 30 minutes and eventually hardened to a red brown solid in 2-3 hours. This solid was readily soluble in DMSO, DMF and pyridine. Repeated extraction of this solid in a Soxhlet extractor with ether, chloroform and methanol separated the unreacted monomers. A significant point here is that this extract contained mostly VP and very little or no TNS. For example, if the monomer feed was equimolar, approximately 50% of the initial charge of VP could be recovered by this procedure. The residue left was further purified by dissolving it in DMF and precipitating with ether.

The polymerization also proceeded spontaneously in solution. The bulk polymerization was always faster than the solution polymerization. This is presumably due to the "dilution effect" of the solvent. Table 8 briefly summarizes the solvent effect on the polymerization. The similarity between this system and the homopolymerization of TNS is at once evident. Polar solvents

favor the reaction indicating the ionic nature of the initiation and/or propagation steps. This phenomenon could also be interpreted in terms of the relative reactivities of the complex and the free monomers. In general, the equilibrium constant of the complex decreases as the solvation increases. Several examples of this are known. The equilibrium constant for the 1,3,5-trinitrobenzene-N,N-dimethylaniline system decreases in the order: cyclohexane>carbontetrachloride >chloroform>1,1,2,2-tetrachloroethane>1,4-dioxane.[6] As the solvation increases, the complex concentration decreases. Thus, the increase in the polymerization rate must largely be the result of the increased efficiency of the initiation step.

Table 8

Solvent Effect of the Copolymerization of TNS and VP

Solvent	Polymer yield[a] in g
THF	0.093[b]
1,2-Dichlorcethane	0.045
Acetonitrile	0.209
DMSO	0.241

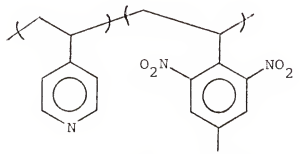
[a]Reaction conditions: 0.3 g TNS (1.25 mmole) and 0.131 g VP (1.25 mmole) in 1 ml of solvent, at room temperature for 48 hours.

[b]Reaction time: 78 hours.

Structure of the TNS-VP Copolymer

A wide variety of structures are possible for the copolymer because of the several modes of polymerization. Some of these possibilities are discussed below.

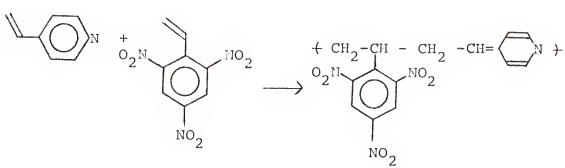
Vinyl Copolymer



IV

This could be alternating or random or block copolymer. The polymerization is strictly through the vinyl groups.

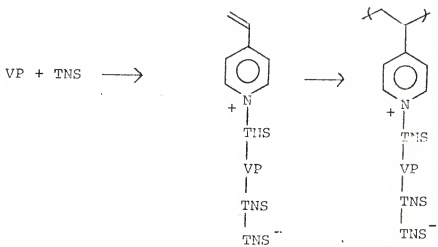
"Ionene"-type Copolymer



V

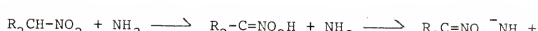
This is conceivable especially in the light of the isolation of product shown in equation 9. Again, there are alternating, random, or block structures possible.

"Graft" Copolymer

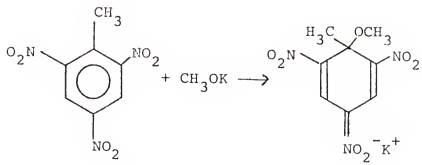


Structure VI

In this case, the initial polymerization is through the vinyl groups of TNS to give a linear copolymer with quaternized pyridinium end-groups. Salamone, et al., have shown that quaternized vinylpyridinium salts are extremely reactive to even mild bases such as pyridine, CN^-, Cl^-, etc.[31] It is then conceivable that in the presence of unreacted VP, the vinyl pyridinium end-groups can undergo further polymerization leading to structure VI. The counterion in this case is the highly stable trinitrobenzylanion which can be converted to the nitronate form. Such nitronic acids are well known and characterized as can be seen from equations 10 and 11.

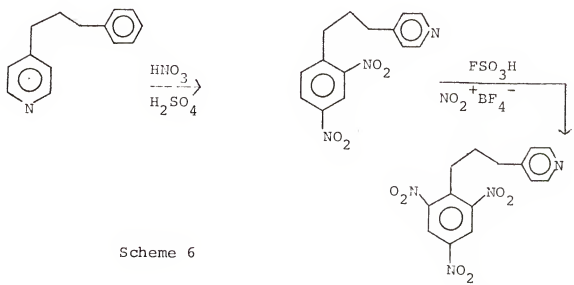


Eq. 10 Ref. 32



Eq. 11 Ref. 33

The structure of the copolymer was determined by comparing the PMR spectrum of the copolymer with several model compounds including poly VP, poly TNS and 4[3-(2,4,6-trinitro)phenyl]propyl pyridine (TNPPP, Structure II). TNPPP was synthesized according to Scheme 6.



Scheme 6

(II)

The ir, pmr and cmr spectra of TNPPP are given in Figures 3 - 5. The spectra of the copolymer and other relevant compounds are given in the subsequent figures.

A cursory comparison of the pmr spectra of the copolymer and poly VP eliminates the possibility of any block copolymer. If VP blocks were present, there should have been a strong methylene absorption at δ ~1.6 ppm but there is none. The protons in the heterocyclic ring in structure V absorb at δ 5.8 and 6.2 ppm in the pmr spectrum. Absence of such absorptions by the copolymer will seem to rule out any significant contribution from "Ionene" -type structures. The pmr spectrum of the copolymer (Fig. 10) shows the absorptions due to the trinitrophenyl and 4-substituted pyridyl groups at δ 9 ppm, 7.2 and 8.2 ppm respectively. The broad peaks in the pmr spectrum also suggest that the copolymer could not have a simple, completely alternating structure. Even at high temperatures (~100°C) the peaks remained substantially broad and did not change appreciably. This behavior could be attributed to some characteristic inherent in the copolymer structure. Structure VI also has quaternized pyridinium groups which show absorptions in the pmr spectrum at δ 8.0 and 8.8 ppm. Coupled with the fact that all of them are segments of a polymer chain, it is reasonable to conclude that absorptions of all the above mentioned groups are indeed present in the spectrum. The methylene absorptions are also correspondingly broad.

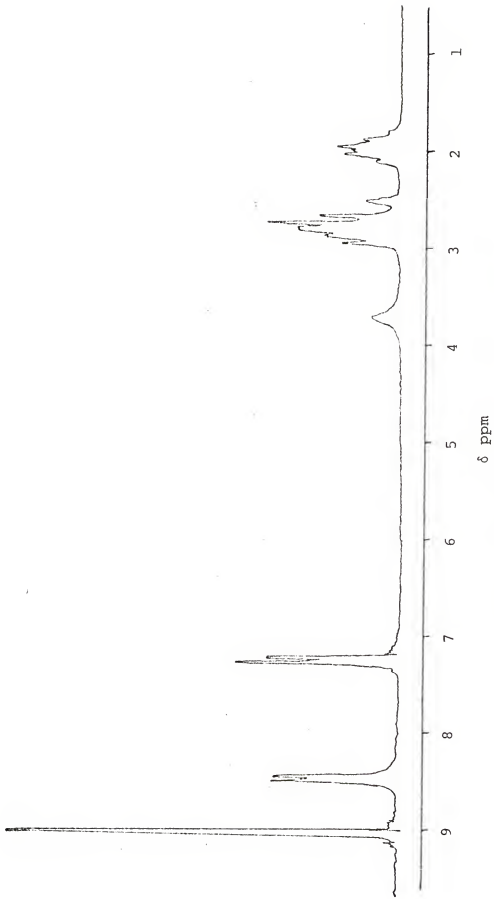


Figure 3: PMR Spectrum of Compound II

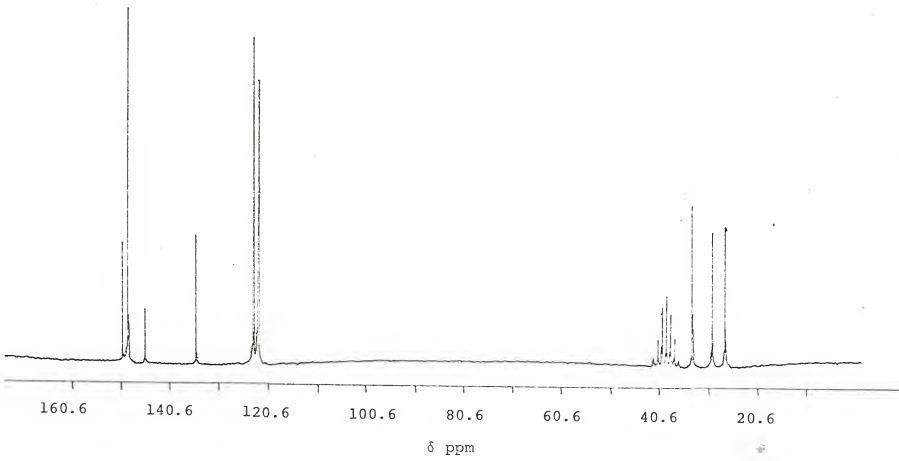


Figure 4: CMR Spectrum of Compound II

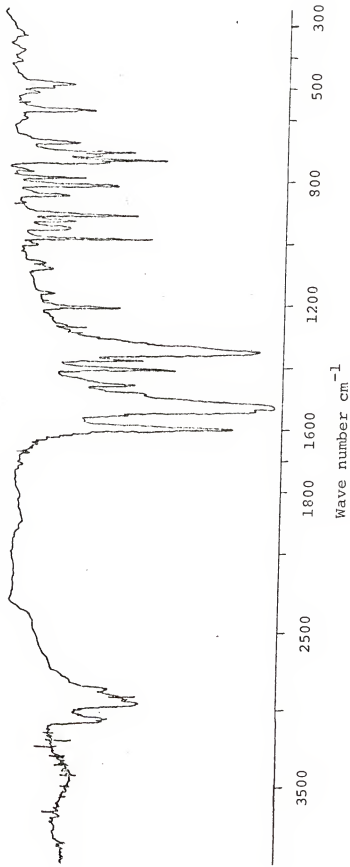


Figure 5: IR Spectrum of Compound II

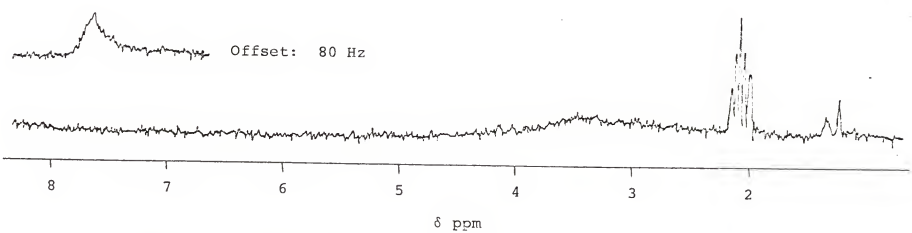


Figure 6: 60 MHz PMR Spectrum of Poly TNS Initiated with Pyridine

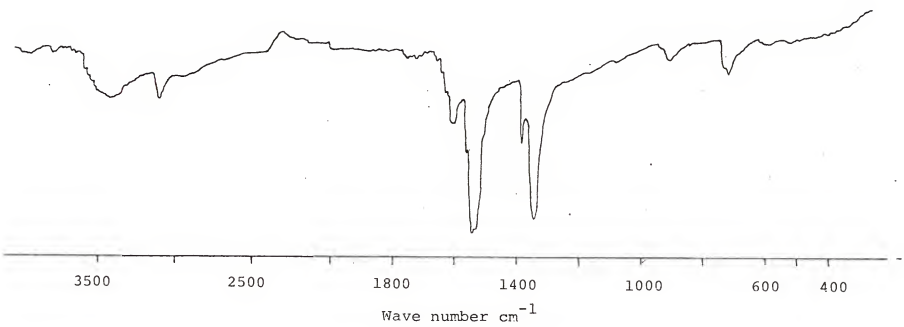


Figure 7: IR Spectrum of Poly TNS Initiated with Pyridine

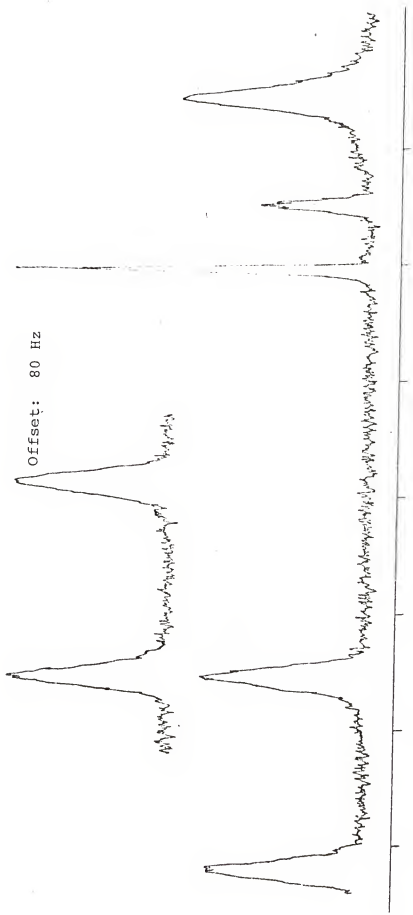


Figure 8: 60 MHz PMR Spectrum of Poly VP

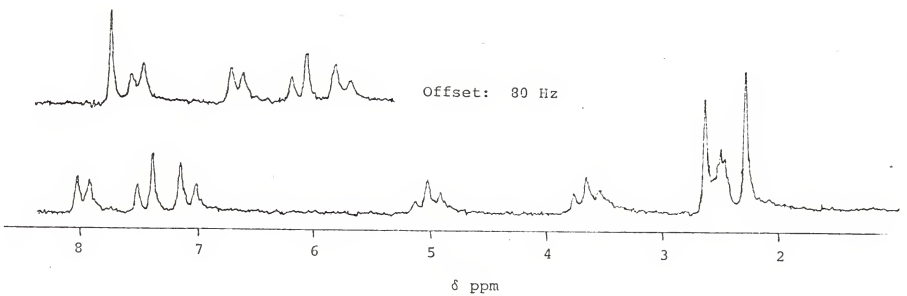


Figure 9: 60 MHz PMR Spectrum of 2-(2,4,6-Trinitrophenyl)ethyl-pyridinium Tosylate (Product in Eq. 9).

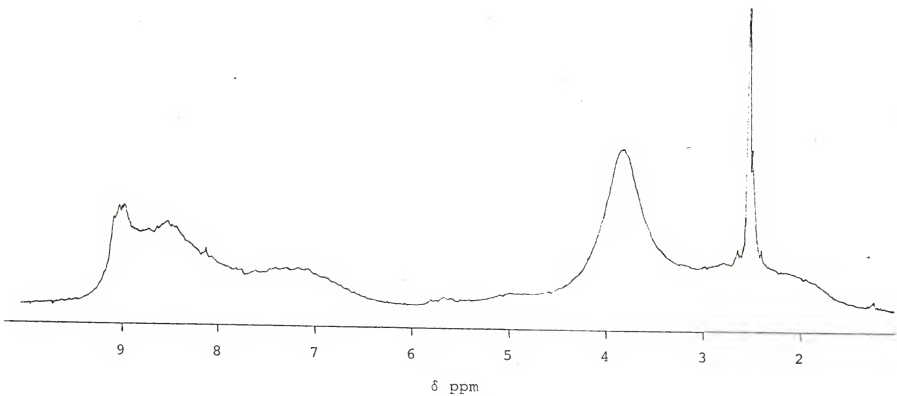


Figure 10: 100 MHz PMR Spectrum of the VP-TNS Copolymer (VP-TNS-640)

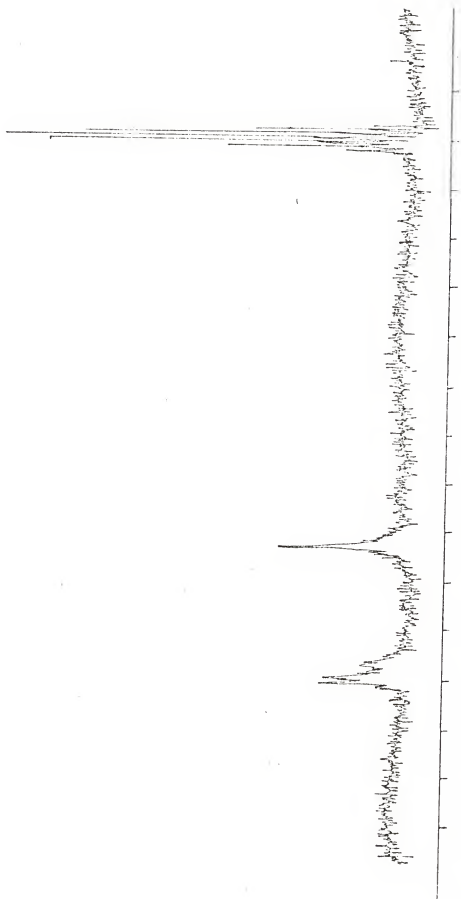


Figure 11: CMR Spectrum of VP-TNS Copolymer (VP-TNS-640)

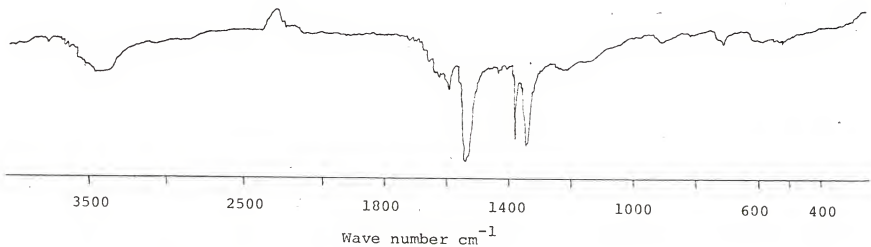


Figure 12: IR Spectrum of VP-TNS Copolymer (VP-TNS-711)

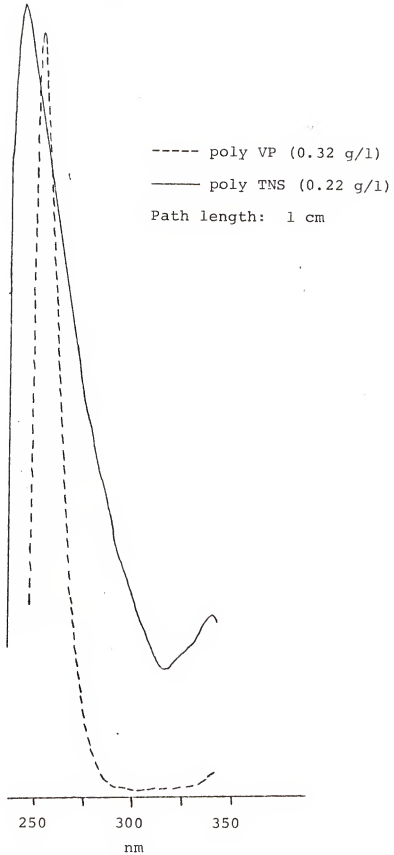


Figure 13: UV Spectra of Poly VP and Poly TNS in DMSO

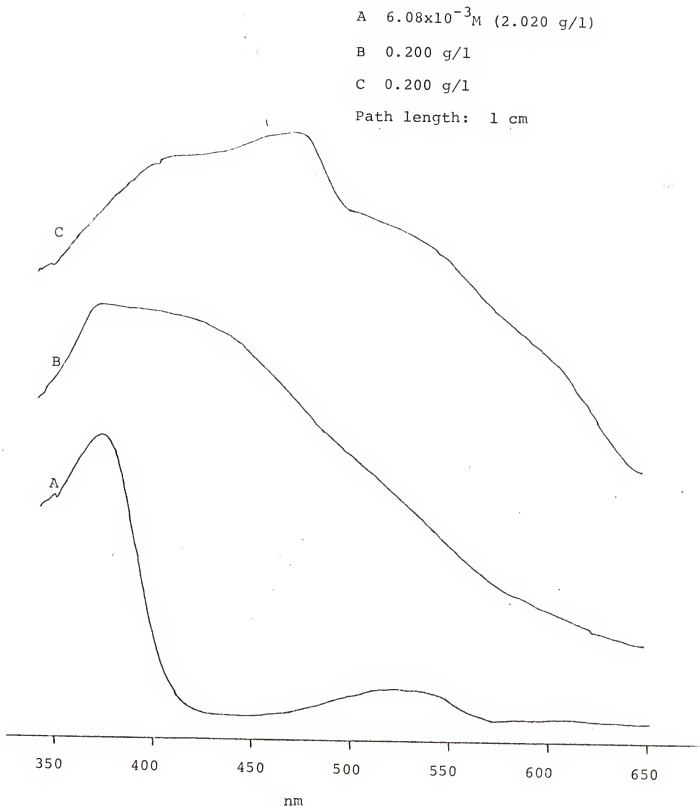


Figure 14: UV Spectra of (A) Structure II, (B) poly TNS, and (C) Copolymer of TNS and VP (VP-TNS-711) in DMSO

Structure VI also differs from structures IV and V by conferring some ionic character on the polymer. The separation of charges will make the polymer act like a polyelectrolyte in studies involving the frictional properties of macromolecules such as solution viscosity. The specific viscosity of a macromolecule in solution is directly proportional to the total volume occupied by the macrocolecule. For a spherical particle, this volume fraction can be correlated with their concentration as shown in equation 12.

$$\eta_{SP} = [\eta]C_2 + k'[\eta]C_2^2 \qquad \text{Eq. 12}$$

where η_{SP} = Specific viscosity,

$[\eta] \equiv \eta_{SP}/C_2$ as $C_2 \rightarrow 0$ = Intrinsic viscosity

C_2 = Concentration of the macromolecule and

k' = Huggin's constant.

Assuming the shape of the polymer chain changes only slightly with dilution, a plot of (η_{SP}/C_2) vs C_2 should be linear with a positive slope. The situation, however, is different for polyelectrolytes. Increasing dilution provides increasing volume for the counterions and this leads to decreased shielding between ions of similar charge. Consequently, the polymer chain expands on dilution and the viscosity thus increases with dilution. For a polyelectrolyte, a plot of (η_{SP}/C_2) vs C_2 usually has a negative slope. Similar behavior should be observed if the structure

Table 9

Viscosity Data for VP-TNS Copolymer (VP-TNS-782)

Concentration, C g/100 ml	"t" sec	$\eta_\gamma (=t/t_o)$	$\eta_{SP} (=\frac{t-t_0}{t_0})$ (x10^2)	η_{SP}/C (x10$_2$)
0.505	439.6	1.021	2.1	4.2
0.287	438.8	1.019	1.9	6.6
0.214	438.8	1.019	1.9	8.9
0.171	440.8	1.024	2.4	14(.0)
0.142	441.5	1.026	2.6	18(.3)
0.121	441.7	1.026	2.6	21(.5)

Solvent: DMF

Temperature: 24.7°C

"t_0" for DMF: 430.5 secs.

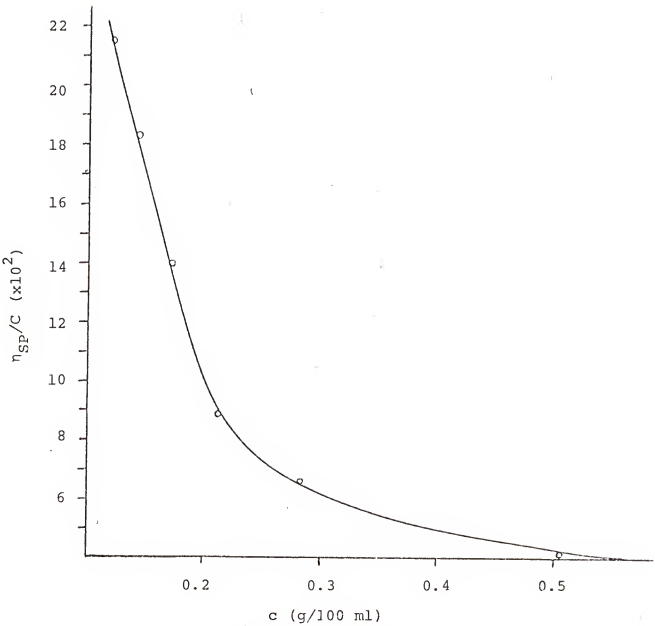


Figure 15: Viscosity Behavior of VP-TNS Copolymer (VP-TNS-782)

of the VP-TNS copolymer is VI. Fig. 15 gives a plot of (η_{SP}/C_2) vs C_2 and the "negative slope" indicates the polyionic character of the copolymer. The low specific viscosity also suggests that the molecular weight of the copolymer is not very high. Taking the spectral and viscosity data into consideration, structure VI seems to be the most reasonable structure for the copolymer.

Composition of the Copolymer

Conventional methods to determine the composition of a copolymer include analyses of the UV, pmr and ir spectra. Both poly VP and poly TNS absorb strongly in the UV region - the former at 266 nm and the latter at 272 nm. The difficulty in resolving these absorptions in the copolymer renders UV spectral data useless for the determination of the composition. The broad absorptions in the "aromatic region" of the pmr spectra lead to considerable overlapping and hence to inaccurate integration of peak areas.[34] Measurements of peak areas are difficult and often unreliable in cmr spectra.[35] The drastic change in band shapes in going from the monomer to the polymer and the lack of reproducibility of spectra make ir spectral data unsuitable for quantitative purposes.[36]

It can be shown that for two monomers A and B with compositions E_A and E_B for a particular element, the composition of the copolymer is given by equation 13.

The accuracy of this method depends on precise and complete combustion techniques. At its best, it can give values

$$\frac{N_A}{N_B} = \frac{M_B(E_B - E_{obs})}{M_A(E_{obs} - E_A)} \qquad \text{Eq. 13}$$

where N_A/N_B is the ratio of the monomers in the copolymer

M_A and M_B are molecular weights of A and B respectively and

E_{obs} = observed composition of an element in the copolymer

within 3-5%. Data from elemental analyses have been used to determine reactivity ratios of monomers. However, some polymers do not give satisfactory analyses. Polyacrylonitrile is one example where special procedures have to be used because at high temperatures it tends to undergo cyclization to give ladder polymers.[37] Poly VP sometimes does not give agreeable analyses but this has been attributed to tightly bound solvent (usually methanol) molecules.[38] To minimize the occurrence of such situations, the copolymers were precipitated from a minimum amount of DMF with large volumes of ether. The absence of any significant amount of DMF in the precipitated polymer is evident from their pmr spectra. Still, the nitrogen analyses were far short of the theoretical values. Apparently, this was due to the difficulty in combusting the nitro groups completely. In all cases, the carbon and hydrogen analyses were internally consistent and averages of the two values were used for the calculation of the composition of copolymers. In some cases, the hydrochloride

derivatives of the copolymers were analyzed for chlorine and were used a verification of the composition calculated from the carbon-hydrogen analyses.

A key experiment to evaluate the participation of the complex in the propagation step is to study the dependence of the composition of the copolymer on the monomer feed-ratio. Invariance will usually mean extensive participation by the complex. The results of such an experiment are given in Table 10. The compositions are the average of the values calculated from carbon and hydrogen analyses using equation 13.

With N-Vinylcarbazole

N-Vinylcarbazole (NVC) is known to form strong complexes with acceptors like chloranil, trinitrobenzene, etc. The work of Tada, et al.,[4] Tazuke[39] and several others has clearly established the participation of such complexes in the initiation and propagation steps. Both ionic and radical polymerizations are possible and the mechanistic route is controlled by the choice of solvents. Less basic solvents like benzene and dichloroethane tend to favor the cationic mechanism whereas basic solvents such as DMSO and acetonitrile favor the radical route. Photoinitiation of NVC systems is also accompanied by the cyclodimerization of NVC.

NVC formed an intense red solution in CH_2Cl_2 with TNS. The UV spectrum of this mixture showed a maximum around 440 nm. Irradiation of an equimolar mixture in

Table 10

Relationship Between VP-TNS Copolymer Composition and Monomer Feed-Ratio

Entry #	Feed Ratio (VP:TNS)	Time of Reaction*	%VP in the Copolymer
VP-TNS-712	1:2	21 hrs	22.4
VP-TNS-711	1:1	0.75 hrs	28.1
		4 hrs	29.3
		21 hrs	27.2
VP-TNS-721	2:1	21 hrs	53.5
VP-TNS-782	8:2	21 hrs	59.4
VP-TNS-791	9:1	21 hrs	58.3

*All polymerizations were done in bulk at room temperature.

[NVC] = [TNS] = 2 M in CH_2Cl_2
Irradiated at 440±12.8 nm for 24 hours.

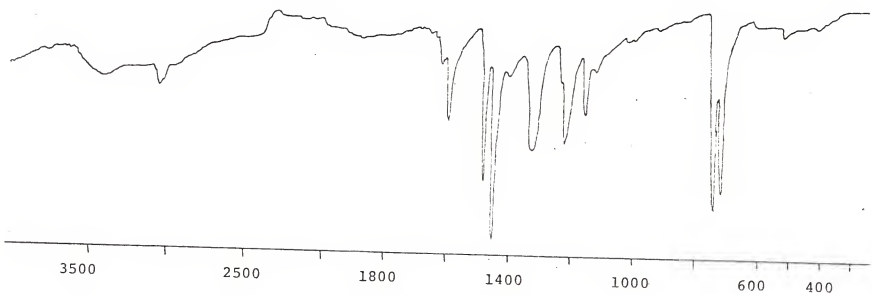


Figure 16: IR Spectrum of the Polymer Obtained on Irradiating NVC and TNS.

CH_2Cl_2 at 440±12 nm for 24 hours gave poly NVC in about 50% yield. The identification of the polymer was made by elemental analysis and comparison of its ir spectrum with that of a standard sample in the Sadtler spectra. An equimolar mixture in acetonitrile under the same conditions yielded poly NVC. Another attempt to copolymerize the two monomers in DMSO with triethylamine as the initiator failed to give any copolymer. Control experiments proved that there was no spontaneous polymerization of any kind in DMSO.

With 2-Vinylnaphthalene

2-Vinylnaphthalene (VN) undergoes anionic polymerization and with styrene forms copolymers.[40] The vinyl group also undergoes nucleophilic reactions with diethylamine, etc.[41] From the equilibrium constant for the model compounds, the complex concentration should also be expected to be high. A mixture of VN and TNS in CH_2Cl_2 developed a greenish yellow color with an absorption maximum at around 425 nm. To avoid excitation of TNS which also absorbs at 425 nm, the VN and TNS mixture was irradiated at 440 nm for 24 hours. The solvents used were acetonitrile and methylene chloride. In either case, no polymerization was observed. An equimolar mixture in DMSO with triethylamine failed to give copolymers.

With 3,5-Dimethoxystyrene

The 3,5-dimethoxystyrene (DMS) dissolved TNS freely to give a greenish yellow solution and on standing, a

greenish yellow precipitate was obtained. This had a low melting point (32-3°C) and showed the presence of DMS and TNS in 1:1 ratio in the nmr spectrum. Various conditions were tried to copolymerize DMS with TNS but proved abortive. Some of them are: thermal initiation with benzoyl peroxide, photodecomposition of AIBN, DMSO solution of an equimolar mixture with pyridine and triethylamine (10%) and n-butyl lithium in benzene at -50°C. No polymer was formed in any of these cases.

With N,N'-Dimethylaminostyrene

In their original report, Yang and Gaoni referred to the spontaneous copolymerization of TNS and dimethylaminostyrene (DMAS). On dissolving TNS in DMAS, an intense red color was produced accompanied by an exothermic reaction. The solution grew more viscous with time and in about 20 minutes gave a red brown solid. Extraction of this solid with ether and methanol removed the unreacted monomers. Nmr of the extracts also showed the presence of some other side products which were not identified because of their low concentration. The crude polymer was soluble in $CHCl_3$ and benzene and was purified by precipitation with hexane from chloroform. Elemental analysis showed the composition to be DMAS:TNS::56:44. Polymers of similar composition were obtained from equimolar mixtures in acetonitrile and methylene chloride. Nmr and ir spectra also showed the presence of the nitro groups. It is not absolutely certain whether or not this is a mixture of poly DMAS and a copolymer of the two.

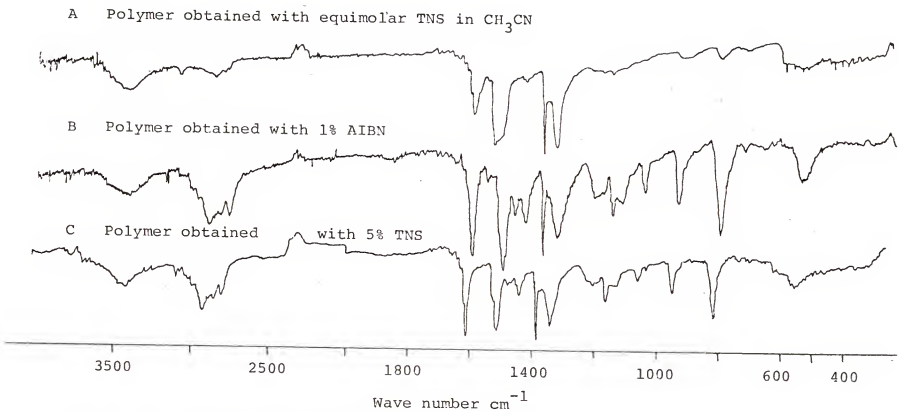


Figure 17: IR Spectra of Polymers Involving DMAS

With a view to clarify the initiation mechanism of the polymerizations involving DMAS, 5% solutions of 1,3,5-trinitrobenzene and TNS were prepared in the pure monomer. The initial mixtures were dark red and both gave polymers after 24 hours. The crude polymers were purified by precipitation from benzene with methanol to give off-white polymers. Elemental analysis and comparison of their ir spectra with that of an authentic sample of poly DMAS confirmed that they were poly DMAS with little incorporation of TNS.

For purposes of convenience, it is perhaps useful to list all the copolymerization data in Table 11.

Mechanistic Implications

Structure of the TNS-Donor Complexes

As mentioned earlier in connection with the TNS-amine systems, conductance measurements can be expected to serve as a measure of the ionic character of complexes in the ground state. If the complexes are largely ionic, high conductivities should be observed in solvents like DMSO. Table 12 gives the relevant data concerning the conductivity measurements. It is clear that the concentrations of ions in the above cases are very low. This will mean that while the "dative" or "charge-transfer" structure is an important element in the stabilization of such complexes, it is probably not an exclusive and accurate character of the complexes. Thus, it is perhaps not correct to assume or propose structures like VII in the propagation step of

Table 11

Copolymerization Behavior of Donor Monomers with TNS

Donor	Polymerization Conditions	Feed Ratio (Donor:TNS)	Result
4-VP	Bulk Polymerizations at room temperature	9:1 - 1:2	Increasing VP content in the copolymer with increasing VP in the monomer feed
DMAS	Bulk and solution polymerization at room temperature	1:1	55-58% of DMAS in the copolymer
	With 5% TNS or TNB		Poly DMAS
NVC	Irradiation at the C-T band in solution at room temperature	1:1	Poly NVC only - no copolymers
VN	Irradiation at the C-T band in solution at room temperature	1:1	No polymers
3,5-DMS	Bulk, solution, radical, anionic polymerizations	1:1	No polymers

Table 12

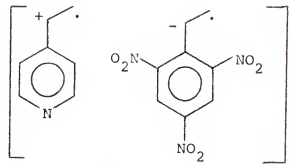
Conductivities of TNS-Donor Complexes in DMSO at Room Temperature

Donor	Concentration of the Donor	Conductivity of the Donor Solution	Conductivity of the Donor and TNS Solution
4-Vinylpyridine	1.29 M	0.4 μ℧	59 μ℧
N-Vinylcarbazole	1.27 M	0.8 μ℧	7.2 μ℧
2-Vinylnaphthalene	1.27 M	1.8 μ℧	7.8 μ℧

Concentration of TNS solution: 1.25 M

Conductance of TNS solution: 2.9 μ℧

the copolymerization.



VII

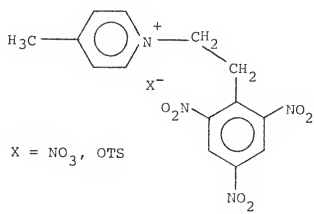
As Ledwith and Hyde[3] have argued, if structures like VII do exist, it is reasonable to expect the formation of substituted cyclobutanes. In all of the above cases, no such products were isolated. Only in the case of DMAS, some side-products were detected in the pmr spectrum. These, however, were present in too small amounts to permit structure evaluation.

Role of D-A Complexes in the Initiation Step

It seems likely that the polymerization is initiated by a D-A complex in the case of the DMAS-VP system. There are both direct and indirect evidence available for this. For example, with 5% TNS or TNB, poly DMAS was formed. The lack of incorporation of TNS or TNB in the polymer was detected in the ir spectrum and was subsequently confirmed by elemental analysis. The indirect evidence comes from the inability of N,N-dimethylamino-p-toluene

to initiate the polymerization of TNS. This would seem to rule out any nucleophilic attack by the amino moiety on TNS.

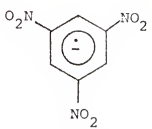
On the other hand, the available data seem to indicate that the copolymerization of VP and TNS proceeds from the nucleophilic attack by the pyridine moiety on the double bond in TNS (See Scheme 3). The isolation of the intermediate (Structure VIII),



VIII

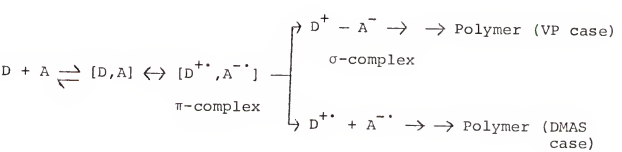
is a strong evidence in favor of such a mechanism. Similar intermediates could not be isolated from a mixture of TNS and VP. This is not very surprising because the double bond in quaternized VP is much more susceptible to nucleophilic attack than VP. In fact, in all the attempts some polymeric material was formed. It is also worth mentioning that no polymer was formed when VP was mixed

with 10% TNB. Even if there was appreciable complex formation, it was not able to initiate the polymerization of VP. The reasons are two-fold: (1) VP does not polymerize cationically and (2) the anion like structure IX, is not capable of initiation of the anionic polymerization of VP because of thermodynamic reasons.



IX

Taking all the data into consideration, it is possible to visualize the following scheme for the initiation mechanism.



Scheme 6

The differences could be rationalized on the basis of:

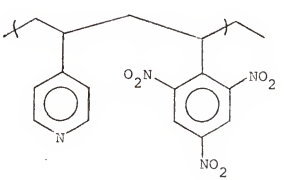
1. The ionization potentials (IP): A good approximation of the IP's of VP and TNS can be made from their corresponding toluenes in Table 6. The IP of DMAS is probably less than that of VP. This will mean that transfer of electron or charge is a much more facile process in the case of DMAS than in the case of VP.

2. The nucleophilicities: Again, Table 6 can be used to conclude VP is more nucleophilic than DMAS. Thus, with VP the initial π-complex formation is followed by the nucleophilic attack on TNS to generate a Zwitterion which is a σ-complex.

The formation of poly NVC in the case of NVC and TNS is undoubtedly initiated by the "dative structure" since the photolysis was carried out at the C-T band where both TNS and NVC do not absorb.

Participation by the Complex in the Propagation Step

Qualitatively, the participation of the complex in the propagation step can be verified from the spectra of the copolymers and from thermodynamic arguments. The pmr spectra of the copolymers indicate the presence of units such as



in the polymer chain. Once the initiating species viz. the

Zwitterion has been generated, both TNS, VP and the complex are free to add to the negative end of the dipole. Comparing TNS and VP, TNS is far more likely to add faster than VP because of the stabilities of the resulting anions (See equations 14 and 15).

$$VP + TNS \rightleftharpoons \overset{+}{VP} - TNS^{-} \xrightarrow{TNS} \overset{+}{VP} - TNS - TNS^{-} \quad \text{Eq. 14}$$

$$\overset{+}{VP} - TNS^{-} \xrightarrow{VP} \overset{+}{VP} - TNS - VP^{-} \quad \text{Eq. 15}$$

The trinitrobenzyl anion is much more stable than the methyl pyridyl carbanion. This is again illustrated by the inability of TNB to initiate the polymerization of VP. Thus, the incorporation of VP in the copolymer must have come through the complex. In the case of the complex, the monomers are in very close proximity and an attack by the growing chain-end on VP can be immediately followed by the formation of the stable TNS^{-} (Eq. 16).

$$\sim\sim\sim TNS^{-} + [VP,TNS] \longrightarrow \sim\sim TNS \cdots VP,TNS \longrightarrow \sim\sim TNS\text{-}VP\text{-}TNS^{-} \quad \text{Eq. 16}$$

Similar arguments can be considered to hold good for the DMAS-TNS system. Quantitative evaluation of the participation by the complex is difficult because of the formation

of both 1:1 and 1:2 (TNS:VP) complexes. The ratio of the concentrations of the two complexes changes with the concentration of VP. For example, at high VP concentrations, the 2:1 complex will predominate and vice versa. The reactivities of these complexes may vary and are hard to estimate. Since the VP content in the copolymer increases with high VP/TNS ratio in the monomer feed, it is reasonable to assume that both the complexes do indeed participate in the polymerization.

From the data on the equilibrium constants on the model compounds, NVC-TNS and VN-TNS systems can be expected to form copolymers. The reason for the failure of copolymer formation can lie in the steric orientation factor. Because of their relatively small size, DMAS and VP can be expected to orient themselves in such a manner as to make the vinyl groups in close proximity. With NVC and VN, this may not be feasible. It is interesting to note in this connection that while NVC forms copolymers through D-A complexes, 2-vinylcarbazole does not show any such tendencies.

CHAPTER 4
EXPERIMENTAL

General Information

Infrared spectra and UV spectra were obtained from a Beckman IR-10 spectrophotometer and a Beckman Acta V spectrophotometer, respectively. Most of the PMR spectra were taken on a Varian A-60 A spectrometer but some of them were taken on a XL-100 spectrometer as were all the CMR spectra. Number average molecular weights were determined on a Mechrolab 302 A Vapor Pressure Osmometer. Viscosity studies were made with a Cannon Ubbelohde semi-micro dilution viscometer. Conductivity measurements were made on a Radiometer conductivitymeter (Type: CDM2e) with a cell (Type: CDCS 6702) of cell constant 1.8 cm. ESR spectra were recorded on a Varian E-9 spectrometer.

Melting points were taken an a Thomas-Hoover Capillary melting point apparatus. All melting points and boiling points are reported uncorrected in degrees centigrade.

Elemental analyses were performed either by Heterocyclic Chemical Corporation, Harrisonville, Missouri, or by PCR, Inc., Gainesville, Florida.

4-VP was obtained from Eastman Kodak Co. and 2-VN, from Polysciences, Inc. Both were purified suitably before use in polymerization studies. All other chemicals and solvents were used as purchased unless otherwise mentioned.

Syntheses of Monomers and Model Compounds

Diethylmethyl-2-(2,4,6-trinitrophenyl)ethyl Ammonium Iodide.

2,4,6-Trinitrotoluene (TNT) (23.2 g, 0.100 mole) was dissolved in 80 ml dioxane and placed in a 250 ml three-necked round-bottomed flask fitted with a thermometer and a reflux condenser. NaOH solution (4.2 ml) was added to it and the mixture cooled to about 0°C in an ice-bath. Diethylamine (7.6 g, 0.10 mole) and 8.8 g (approximately 0.10 mole) of 37% aqueous formaldehyde were mixed at 0°C separately and the mixture added to the TNT solution dropwise. After the addition was complete, the reaction mixture was stirred in the ice-bath for 1 hour and then warmed at 40-50°C for 2 1/2 hours. It was then cooled in an ice-bath and poured into about 300 ml cold water. The resulting oil and the aqueous solution were repeatedly extracted with ether. The ethereal solution was dried over anhydrous $MgSO_4$ and stripped of the ether. A dark red oil was obtained which on mixing with an equal amount of CH_3I gave orange crystals. These crystals started forming in about 20 minutes but the mixture was let stand for 24 hours. Recrystallization from 50% ethanol-methanol mixture gave 26.1 g (56.2% yield) of bright orange crystals, m.p. 130-1°C. The nmr spectrum (D_2O) gave signals at δ 9.2 ppm (singlet), 3.6 ppm (broad multiplet) 3.2 ppm (singlet) and 1.4 ppm (triplet).

2,4,6-Trinitrostyrene

Diethylmethyl-2-(2,4,6-trinitrophenyl)ethyl ammonium

iodide (4.6 g) was dissolved in 100 ml of methanol and 100 ml water. Silver oxide (5 g) was added to it with vigorous stirring. The blood-red solution was filtered after one minute through a Celite pad and washed down with water until the washings were colorless. The solution was set aside for at least 24 hours when shiny pink crystals of 2,4,6-trinitrostyrene were formed. These were recrystallized from benzene-petroleum ether to give 0.8 g (33 % yield) of the bright yellow trinitrostyrene, m.p. 62-3°C. The nmr spectrum (Acetone-d_6) gave signals at δ 9.05 ppm (singlet), 7.1 ppm (quartet) and 5.6 ppm (quartet).

3,5-Dimethoxystyrene

Triphenylmethylphosphonium bromide (107.1 g, 0.3000 mole) was suspended in 1200 ml of anhydrous ether in a 2 l three-necked round-bottomed flask fitted with a reflux condenser, a mechanical stirrer, a N_2 inlet tube, a rubber septum and an addition funnel. To this suspension in ice-bath was added 140 ml of n-butyl lithium (20.2% solution in hexane) in small portions. The yellowish orange ylid was stirred at room temperature for 4 hours and mixed with 49.8 g (0.3 mole) of 3,5-dimethoxybenzaldehyde which was added dropwise over a period of 30 minutes. The white reaction mixture was stirred at room temperature for 8 hours and finally with 1000 ml water for 30 minutes. The ether layer was separated and the aqueous solution was extracted with ether. The two

ether solutions were mixed, dried over anhydrous $MgSO_4$ and stripped of the ether in the rotary evaporator. The yellowish liquid was distilled at 72°C/0.55mm to give 19.7 g (40% yield) of the clear, colorless 3,5-dimethoxystyrene. The nmr spectrum (CCl_4) showed signals at δ 6.8, 6.6, 6.4 ppm (multiplets), 5.55 ppm (quartet) and 3.75 ppm (singlet).

N,N-Dimethylaminostyrene

To 10.17 g (0.03000 mole) of triphenylmethyl phosphonium bromide suspended in 80 ml THF, 24 ml (approximately 0.050 mole) of 20.2% n-butyl lithium in hexane was added. The orange solution was stirred at room temperature for 4 hours and treated with a solution of 4.5 g (0.03 mole) of p-N,N-dimethylamino benzaldehyde in 25 ml THF, added dropwise. The yellowish white slurry was stirred for 8 hours at room temperature and then with 100 ml water for 20 minutes. The oil was separated from the aqueous solution which was extracted with ether. The ethereal solution and the oil were mixed, and cooled to 0°C when triphenyl phosphine oxide precipitated. This was filtered out and the solution was stripped of the solvents. The dark yellow liquid was distilled by dropping it into a flask at 140°C at 0.5 mm. The pure styrene had a yellowish tinge and gave the following nmr signals (CCl_4): δ 7.1 ppm (multiplet), 6.6 ppm (multiplet), 5.1 ppm (quartet) and 2.73 ppm (singlet). Yield of the dimethylamino styrene: 60%.

3,5-Dimethoxytoluene

3,5-Dihydroxytoluene monohydrate (45 g (0.32 mole) was placed in a 1 liter round bottomed flask and mixed with 28 g (0.70 mole) of NaOH in 300 ml water. To this solution at 0°C was added dropwise 83.2 g (0.66 mole) of dimethylsulfate and the mixture was refluxed for 3 hours. At the end of the reaction period, it was cooled and poured over 600 ml water. The aqueous solution was extracted with ether. The ethereal solution was washed with dilute H_2SO_4 and then with water, dried and stripped of the ether. The crude oil on distillation at 110°C/12mm gave a clear colorless liquid, 32 g (67% yield). The nmr spectrum in CCl_4 gave peaks at δ 6.3 ppm (singlet), 3.58 ppm (singlet) and 2.2 ppm (singlet).

4-[3-(2,4-Dinitrophenyl)propyl]-pyridine

Fuming nitric acid (25 ml) and 35 ml of concentrated sulfuric acid were mixed carefully and cooled in an ice-bath. 4-(3-Phenylpropyl)-pyridine (20 g, 0.10 mole) was dissolved in 20 ml glacial acetic acid and added slowly to the nitrating acid mixture. After the addition was complete, the ice-bath was removed and the solution was refluxed at 80-90°C for 4 hours. It was then poured into about 200 ml of ice-water, neutralized with aqueous NH_3 to precipitate the crude product. It was filtered, washed several times with water, dried and purified by dissolving in benzene and reprecipitating with petroleum ether. The resulting 4-[3-(2,4-dinitrophenyl)propyl]-

pyridine (25.2 G; 87.8% yield) was quite pure and was recrystallized from aqueous ethanol, m.p. 76.5-77.5°C. The nmr spectrum (acetone-d_6) showed peaks at δ 8.7 ppm (doublet), 8.5 ppm (multiplet), 7.9 ppm (doublet), 7.25 ppm (doublet), 2.95 ppm (multiplet) and 2.1 ppm (multiplet).

Elemental analysis: Calculated: C, 58.53%; H, 4.56%; N, 14.62%. Found: C, 58.29%; H, 4.86%; N, 14.75%.

4-[3-(2,4,6-Trinitrophenyl)propyl]-pyridine

Dinitrophenylpropyl pyridine (8.61 g, 0.0300 mole) was dissolved in 20 ml fluorosulfonic acid under nitrogen in a dry ice-isopropanol bath. Nitronium tetrafluoroborate (11.9 g) was added to the solution gradually under nitrogen. The mixture was then refluxed at 135°C for 3 hours at the end of which it was poured into about 100 g of ice. The solution was carefully neutralized with saturated Na_2CO_3 solution and the crude product was filtered, washed with water and dried. Dissolving it in benzene and reprecipitating with petroleum ether separated an oil which nmr showed to contain some tetranitro compound. The crude 4-[3-(2,4,6-trinitrophenyl)propyl]-pyridine was recrystallized from 95% aqueous ethanol, m.p. 148-150°C. Elemental analysis: Calculated: C, 50.61%, H, 3.64%, N, 16.86%. Found: C, 50.89%; H, 3.80%; N, 16.75%. The nmr spectrum gave signals (acetone-d_6) at δ 9 ppm (singlet), 8.48 ppm (doublet), 7.25 ppm (doublet), 2.95 ppm and 2.1 ppm (multiplets).

Reaction of Trinitrostyrene with Diethylamine

Trinitrostyrene (0.7174 g, 3.000 mmole) was dissolved in 1 ml of the solvent (dioxane or acetonitrile) and added dropwise over a period of 45 minutes to a solution of diethylamine (0.219 g, 3.000 mmole) in 2 ml of the solvent (acetonitrile or dioxane) at 0°C. The mixture was then stirred at room temperature. At the end of the reaction period (1 hour in the case of acetonitrile; 24 hours in the case of dioxane), the solution was poured over ice, extracted with ether, dried over anhydrous $MgSo_4$ and stripped of the solvent. The resulting amine on treatment with an equal amount of methyl iodide gave the corresponding quaternary salt in 50-55% yield of orange crystals, m.p. 128-130°C.

Reaction of 4-Picoline with TNS and 4-Toluene Sulfonic Acid

The procedure was similar to that used by Salamone, et al. in connection with 4-vinylpyridinium tosylate.[29] TNS (100 mg) was added with stirring to 10 ml of picoline and 200 mg of 4-toluene sulfonic acid. The dark purple solution was stirred for 2 hours at room temperature and poured into 60 ml anhydrous ether. The purple precipitate was filtered, dried and dissolved in 15 ml hot methanol to gave a pale pink solution. The methanol solution was concentrated to 2-3 ml and poured into ether. The pale pink solid was then precipitated from methanol with chloroform to give 100 mg of the pure salt (about 49% yield) shown in Equation 9. The NMR spectrum of this compound is shown in Fig. 9.

Polymerizations of TNS

General Procedure

A typical polymerization of TNS in DMSO is as follows. Pure TNS (0.7174 g, 3.000 mmole) was dissolved in 1 ml of DMSO purified by standard procedure. To this light brown solution 0.042 ml (0.0304 g; 0.300 mmole) of previously purified triethylamine was added. The solution immediately became purple which turned to dark red-brown in about 10 minutes. The mixture was stirred at room temperature for 24 - 72 hours and poured into water. The dark brown precipitate (1.004 g) was collected. This crude polymer was placed in an extraction thimble and then in a Soxhlet extractor. It was extracted with ether and then with chloroform. These solvents removed unreacted TNS and some other impurities of low molecular weight. The residue was dissolved in acetone and precipitated with ether to give 0.50 g of a brown solid which was dried in vacuo at 56°C for 2 - 3 days. The nmr spectrum of this compound in DMSO-d_6 is given in Fig.

Analysis: Calculated for $C_8H_5N_3O_6$: C, 40.18%; H, 2.10%; N, 17.57%. Found: C, 40.38%; H, 2.18%; N, 15.43%. The nitrogen analysis was repeated by combusting the sample at a higher temperature with gradual combustion. The % N reported was 17.34%. (Analyst: Hetchem Corp.).

The procedure was exactly identical with other initiators like tributylamine, pyridine, triphenylphosphine,

etc. For initiation using NaCN/DMF, a saturated solution of NaCN in DMF was prepared and to 1 ml of this solution 0.5000 g (2.091 mmole) of TNS was added. The work-up was the same as in the case of triethylamine. For initiation with t-$ButO^-$/t-butanol, the initiator was prepared as follows: Sodium metal (0.2284 g) was dissolved and stirred with 15 ml of pure tert-butanol under nitrogen. After 4 hours of stirring at room temperature, the cloudy solution was filtered and stored under nitrogen. Titration with standard HCl solution showed that 1 ml of this solution contained 0.376 mmole of t-butoxide. This solution (0.28 ml) was diluted with 0.72 ml of DMSO and 0.5000 (2.091 mmole) of TNS was added to it. The initiator concentration was calculated to be 5% of the TNS feed. The work-up was the same as in the other cases.

Polymerization of TNS in Different Solvents

The solvents used were 1,4-dioxane, THF, 1,2-dichloroethane, acetonitrile and DMSO and were purified by methods found in p 429 of The Chemist's Companion by A.J. Gordon and R.A. Ford, John Wiley & Sons, New York, 1972. The initiator used was triethylamine in all cases and was 10% of the TNS feed. Typically, 0.500 g (2.091 mmole) of TNS was dissolved in 1 ml of the solvent and 0.03 ml (0.2 mmole) of triethylamine was added. After 24 hours, all the solutions were poured into water containing a little conc. H_2SO_4. The oil obtained was separated from the aqueous solution and solidified by treating it with

ether. Stirring for 30 - 40 minutes removed unreacted TNS. This procedure was repeated again and the solid obtained was collected and dried. The yields of polymer obtained and % conversion are reported in Table 2.

Polymerization of TNS at -17°C

The solvent used in this polymerization was acetonitrile which was purified by distilling over P_2O_5 and taking the middle fraction, TNS (0.7177 g, 3.001 mmole) was dissolved in 1.5 ml of acetonitrile taken in a clean sample vial and mixed with 0.0142 g (0.140 mmole, 4.7%) of triethylamine. The vial was immediately placed in a long tube containing isopropanol. The exact set-up is shown in Fig. 18.

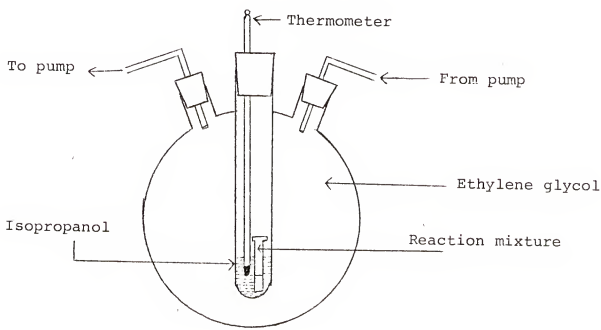


Figure 18: Set-up for the Polymerization of TNS at -17°C

The 3-necked round-bottomed flask was connected to the pump in Precision Lo-Temprol made by Precision Scientific Co. Ethylene glycol was cooled to -17°C and circulated through the flask by means of the pump. The reaction was thus done at -17°C for 65 hours at the end of which the mixture was poured into water containing a little conc. H_2SO_4. The rest of the work-up was the same as above. From the ether extract, 0.4971 g (69.26% of the initial feed) of TNS was isolated. The crude polymer was precipitated once from acetone with water, collected and dried at 56°C under vacuo for 3 days. Yield of polymer: 0.0942 g (13% conversion).

Copolymerizations of TNS With 4-Vinylpyridine

General procedure for the bulk copolymerization of TNS and VP. - 4-VP was distilled under reduced pressure over KOH. The middle fraction which distilled over at 45°C/4 mm was used in all the experiments. The following is a sample procedure for the copolymerization of an equimolar mixture of TNS and VP. TNS (0.7174 g, 3.000 mmole) was weighed into a sample vial and mixed with 0.3208 g (3.051 mmole) of VP. The solution immediately turned dark purplish red in color. It became increasingly viscous with time and eventually solidified into a red-brown solid after 2 - 3 hours. After 24 hours at room temperature, this solid was extracted in a Soxhlet extractor with ether, chloroform and methanol.

The ether extract contained VP and TNS as revealed by the nmr spectrum. A rough calculation from the peak intensities in the nmr spectrum showed that about 50% of VP could be recovered this way. There was very little of TNS. The chloroform and methanol extracts contained a small amount of VP and no TNS. This crude polymer was twice precipitated from DMF with ether. The dark chocolate brown solid was filtered and dried at 80°C in vacuo for 3 days. Yield of copolymer: 0.5034 g. The nmr and ir spectra of this copolymer are in Figures 10 and 12.

Analysis: Calculated for 1:1 copolymer: C, 52.33%; H, 3.513% ; N, 16.27%. Found: C, 45.60%; H, 2.77%; N, 13.67%. Using equation 12, the VP:TNS in the copolymer was calculated to be 26.40:73.60 based on C analysis and 27.89:72.11 based on H analysis. The N analysis always gave low N content. The reason for this is not known.

Copolymerization of VP and TNS in different solvents. - The solvents used were THF, 1,2-dichloroethane, acetonitrile and DMSO which were purified as mentioned earlier. Typically, 0.301 g (1.25 mmole) of TNS and 0.134 g (1.25 mmole) of VP were mixed in 1 ml of solvent and kept at room temperature for 48 hours. In the case of THF, the reaction time was 78 hours. In all instances, the yellow or yellow-brown solutions of TNS turned red-brown on adding the VP. At the end of the reaction time, the mixture was poured into water. The precipitated polymer was collected, dissolved in pyridine and reprecipitated

with ether. The polymer was then dried in vacuo and weighed. The polymer yields in all cases are recorded in Table 8.

Copolymerization of TNS and VP with different feed ratios. - All the polymerizations were carried out in bulk at room temperature for 21 hours. The total concentration of the monomers was held at 6 mmole. In a characteristic run, the TNS was weighed into a sample vial and the appropriate amount of VP was added. In all the cases, an intense dark red color developed instantaneously. Depending on the TNS content in it, the reaction mixture solidified in 0.5 - 4 hours. The mixture with 90% VP never solidified and remained a viscous liquid. At the end of the reaction period, the solid was dissolved in DMF and precipitated with ether. The precipitate was extracted with ether, chloroform and methanol and reprecipitated from DMF with ether. The polymer was then dried in vacuo at 0°C for 3 days. Table 13 gives the details of the polymerizations and analyses of the copolymers obtained.

Copolymerization of VP and TNS at different conversions. - The copolymerization of VP and TNS was stopped after different reaction times and the polymers were analyzed with pmr and cmr spectra. All mixtures were equimolar and after the appropriate time, all were poured into water. The precipitated polymers were extracted with hexane, ether and chloroform and purified

Table 13

Polymerization of VP and TNS with Different Feed Ratios

Entry #	Feed Ratio VP:TNS	Polymer Yield mg	Polymer Yield Wt. %	Elemental Analysis %C	%H
VP-TNS-711	50.4:49.6	0.5034	48.49	45.60	2.77
VP-TNS-712	33.4:66.6	0.4360	37.35	45.01	2.58
VP-TNS-721	67.0:33.0	0.4013	44.36	52.41	3.79
VP-TNS-782	80.4:19.6	0.3591	44.70	56.90	3.78
VP-TNS-791	90.0:10.0	0.1506	21.20	55.25	3.86

as before. Only the samples 675 and 640 were analyzed for C and H. All the data are shown in Table 14. There were some interesting trends in this series of runs. Firstly, the amount of unreacted TNS recovered decreased with time. Secondly, the samples 675 and 615 were soluble in acetone unlike the rest which were soluble in DMF. Thirdly, the samples 675 - 622 were viscous liquids while samples 630 - 600 were hard solids.

Preparation of the HCl derivatives of copolymers. - HCl gas was generated by taking 120 g (2 moles) of sodium chloride and adding 100 ml of conc. H_2SO_4 dropwise over a period of an hour. The acid-salt mixture was shaken occasionally. The gas so generated was dried by passing through conc. H_2SO_4 and bubbled through a DMF solution containing the copolymer. Usually, 0.25 - 0.30 g of the copolymer was dissolved in 4 - 5 ml of DMF and treated with HCl. Control experiment was done by taking 0.5 g of pol-VP in 4 ml DMF. It was observed that at least 92% of the pyridine rings were protonated. With the copolymers, the procedure was repeated once more and the resulting polymers were analyzed for chlorine.

With N,N-Dimethylaminostyrene (DMAS)

Bulk copolymerization. - TNS (0.3001 g, 1.25 mmole) was weighed into a sample vial and 0.1834 g (1.25 mmole) of DMAS was added. The mixing was exothermic and produced a purple-red color. After 25 minutes, it solidified. At the end of 19 1/2 hours, this solid was extracted

Table 14

Copolymerization of VP and TNS at Different Conversions

Run #	Reaction Time Hours	Polymer Yield Wt. %	Elemental Analysis %C	%H
VP-TNS-675	0.75	28.56	46.05	2.77
VP-TNS-615	1.50	37.03		
VP-TNS-622	2.15	66.91		
VP-TNS-630	3.00	54.32		
VP-TNS-640	4.00	74.01	46.31	3.05
VP-TNS-660	6.00	58.96		

Table 15

Chlorine Analyses of Copolymers After Treatment with HCl

Entry #	%Cl	Composition of Copolymer, VP:TNS
VP-TNS-675	2.41	15.2:84.8
VP-TNS-660	2.65	16.7:83.3
VP-TNS-711	4.82	28.7:71.3
VP-TNS-721	4.24	25.6:74.4
VP-TNS-712	3.77	23.04:74.4

with ether and methanol. These extracts contained unreacted TNS and DMAS besides a lot of other unidentified products. The crude solid was dissolved in benzene and precipitated with methanol. Average yield of polymer: 0.0555 g (14.5% by weight). The polymer was brown in color, and was soluble in chloroform, benzene, acetone and DMSO but insoluble in ether, methanol and hexane. Nmr of this compound showed broad peaks at δ 8.9 ppm, 6.5 ppm and 2.9 ppm. Ir spectrum showed absorbances at 1610 cm^{-1} (broad, s), 1530 cm^{-1} (broad, s) 1380 cm^{-1} (s), 1350 cm^{-1} (s) and 820 cm^{-1} (broad, medium).

Analysis: Calculated for 1:1 copolymer: C, 55.96%; H, 4.70%; N, 14.50%. Found: C, 55.49%; H, 4.60%; N, 9.74%.

From the available data, it might be inferred that there is a copolymer but not with a 1:1 alternating structure.

Solution polymerization. - Acetonitrile and methylene chloride were used as the solvents. DMAS (0.1865 g, 1.267 mmole) and 0.3011 g (1.259 mmole) of TNS were dissolved in 0.4 ml of the solvent and reacted for 48 hours. The dark red solution was dissolved in acetone and poured into hexane to give a black oil. On roto - evaporating, this oil gave 0.3705 g of a fluffy orange solid which was extracted with ether and methanol. The crude polymer was dissolved in methylene chloride and precipitated with petroleum ether. Yield of polymer: 0.0425 g (8.71% by weight). Ir showed the presence of

nitro groups and the dimethylamino benzene group.

Analysis: With CH_2Cl_2 as solvent: C, 57.47%; H, 4.98%; N, 9.44%. With CH_3CN as solvent: C, 57.87%; H, 4.87%; N, 13.77%.

Polymerization of DMAS with 5% TNS. - TNS (0.015 g, 0.0652 mmole) was dissolved in 0.1858 g (1.262 mmole) of DMAS. The viscous semi-solid obtained after 24 hours was worked up as before to yield 0.0564 g of the polymer. Ir spectrum of this compound is given in Fig. 17.

Analysis: Calculated for poly-DMAS: C, 81.58%; H, 8.90%; N, 9.51%. Found: C, 81.85%; H, 8.62%, N, 9.83%.

With N-Vinylcarbazole (NVC)

Photopolymerization attempt. - TNS (0.478 g, 2.000 mmole) was weighed into a polymerization tube and mixed with 0.3860 g (1.997 mmole) of NVC and 2 ml of CH_2Cl_2. The tube was subjected to the "freeze-thaw" cycle three times under vacuum to expell all the dissolved oxygen. Then the tube was sealed and the bright red solution was irradiated for 24 hours at 440 ± 12.8 nm with a slit width of 4 mm. The tube was kept at 2 cm from the light source which was a Schoeffel 2500 W Hg-Xe lamp. At the end of the reaction time, the solution was orange and when poured into 30 ml methanol, it gave a yellowish white precipitate. On extraction with ether, it gave a white solid which was purified by dissolving in benzene and precipitating with methanol. Yield of polymer: 0.1805 g.
Ir spectrum of this solid showed absorbances at 3060 (w), 1600 (m), 1485 (s), 1455 (s), 1330 (s), 1225 (s), 1160 (m),

745 (s), and 720 (s) cm^{-1}.

Analysis: Calculated for poly-NVC: C, 87.01%; H, 5.74%; N, 7.25%. Found: C, 87.25%; H, 6.03%; N, 7.30%.

The procedure was similar when acetonitrile was used as the solvent. Yield of poly-NVC: 0.2710 g.

Photocopolymerization Attempt with 2-Vinylnaphthalene (VP)

VN (0.3084 g, 2.00 mmole) and 0.4753 g (2.00 mmole) of TNS were dissolved in 2 ml of methylene chloride in a polymerization tube. The greenish-yellow solution was subjected three times to the "freeze-thaw" cycle and sealed. The tube was placed 2 cm away from the Schoeffel 2500 W Xe-Hg lamp in the photometer and irradiated for 40 hours at 440 ± 12.8 nm. The slit width: 4 mm. At the end of the reaction period, it was poured into 30 ml methanol. No precipitate was obtained. On stripping the methanol off, a viscous yellow liquid was obtained which showed the absorption of vinyl protons due to TNS and VN in the nmr spectrum. A similar procedure with acetonitrile as the solvent gave the same result.

Complexes between 2,4,6-Trinitrotoluene and Donors

The solvent used in all cases were Spectrograde CH_2Cl_2. The UV spectral measurements were taken on a Beckman Acta V Spectrophotometer using a 1 cm cell. In all cases, the absorption of the acceptor was effectively subtracted by using the acceptor solution as the reference. In the case of dimethoxytoluene, nmr was used to determine the equilibrium constant. Varian A-60A nmr

spectrometer was used for that purpose. The equations used were the Benesi-Hildebrand equation for the UV method[42] and the Hanna-Ashbaugh equation for the nmr method.[43] The relevant data appear in the appropriate tables and figures in the text.

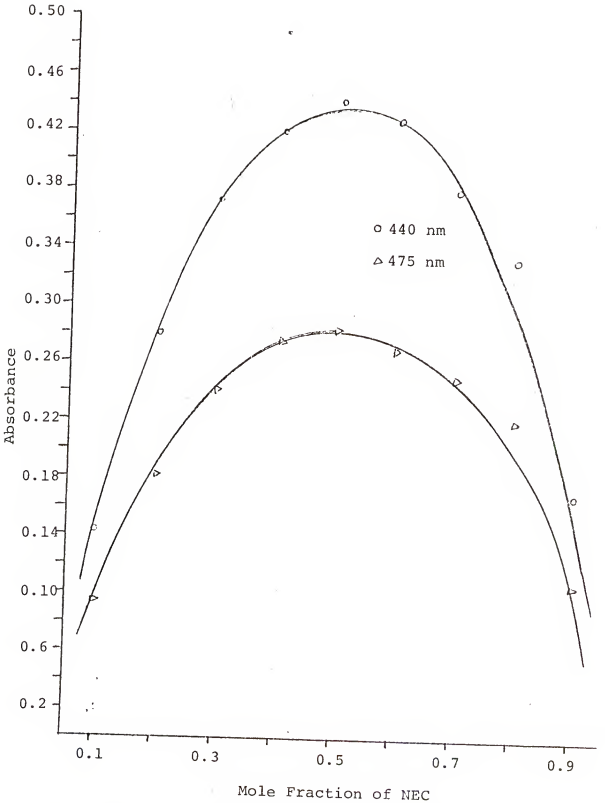


Figure 19: Stoichiometry of the NEC-TNT Complex in CH_2Cl_2

Table 16

Determination of the Equilibrium Constant of the Complex Between N-Ethylcarbazole (NEC) and TNT

$[D_0]$ (M)	$1/[D_0]$	A (absorbance at 475 nm)	$[A_0]/A$ ($\times 10^3$)
0.05182	19.30	0.141	23.63
0.1008	9.921	0.276	12.39
0.1510	6.622	0.400	8.408
0.2012	4.970	0.476	7.278
0.2515	3.976	0.582	6.109
0.2997	3.334	0.688	5.233
0.3440	2.907	0.810	4.415

$[A_0] \equiv [TNT] = 2.682 \times 10^{-2}$ M.

$[D_0] \equiv [NEC]$

Equation used: $\frac{[A_0]}{A} = \frac{1}{K\epsilon_{AD}} \cdot \frac{1}{[D_0]} + \frac{1}{\epsilon_{AD}}$ Ref. 42

Where $[A_0]$ = Concentration of the acceptor.
$[D_0]$ = Concentration of the donor
ϵ_{AD} = Molar absorptivity of the complex.
K = Intercept/Slope = 0.72(3) 1 $mole^{-1}$
Correlation Coefficient: 0.999

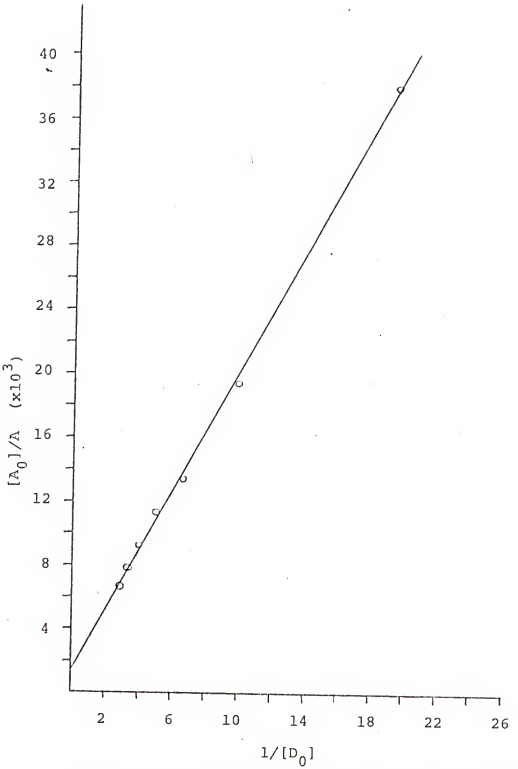


Figure 20: Equilibrium Constant for the NEC-TNT Complex in CH_2Cl_2

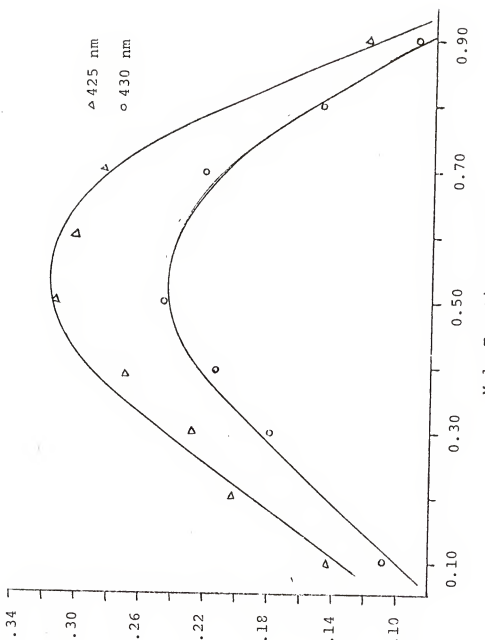


Figure 21: Stoichiometry of the MEN-TNT Complex in CH_2Cl_2

Table 17

Determination of Equilibrium Constant of the Complex Between 2-Methylnaphthalene (MEN) and TNT

$[D_0]$ (M)	$1/[D_0]$	A (absorbance at 425 nm)	$[A_0]/A$ ($\times 10^2$)
0.1006	9.94	0.065	7.80
0.1525	6.56	0.096	5.28
0.2013	4.97	0.117	4.33
0.2531	3.95	0.138	3.67
0.3050	3.28	0.176	2.88
0.3538	2.83	0.185	2.74

$[A_0] \equiv [TNT] = 2.535 \times 10^{-2} M$

$[D_0] \equiv [MEN]$

Equation used is the same as in the case of NEC.

K = Intercept/Slope = 0.99(4) l $mole^{-1}$.

Correlation Coefficient:0.998

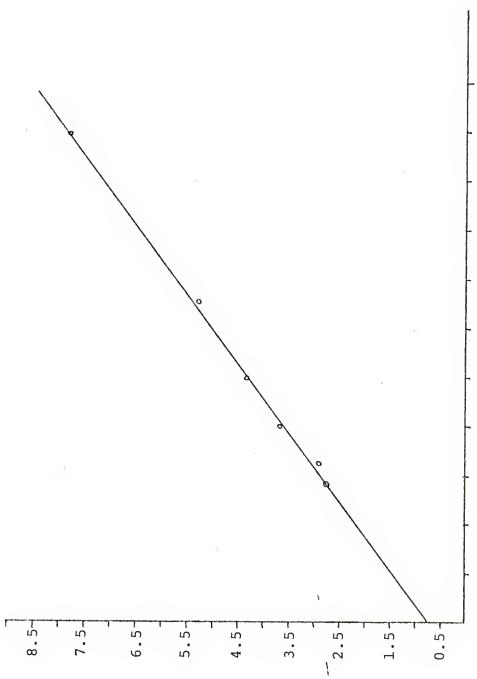


Figure 22: Equilibrium Constant of the MEN-TNT Complex in CH_2Cl_2

Table 18

Determination of the Equilibrium Constant of the Complex Between 3,5-DMT and TNT

[D] (M)	$1/[D]\,(M^{-1})$	δ_A (HZ)	Δ^A_{Obsd} (HZ)	$1/\Delta^A_{Obsd}$ $(x10^2)HZ^{-1}$
0	-	530.5	-	-
3.419	0.2925	508.5	22.0	4.54
2.872	0.3482	511.0	19.5	5.13
2.325	0.4301	515.0	15.5	6.45
1.778	0.5624	518.0	12.5	8.00
1.368	0.7310	519.5	11.0	9.09
0.5471	1.828	526.0	4.5	22.2

[D] = [DMT] [TNT] = $7.03x10^{-2}$M.

Equation used: $\frac{1}{\Delta^A_{Obsd}} = \frac{1}{K\Delta^A_{AD}} \cdot \frac{1}{[D]} + \frac{1}{\Delta^A_{AD}}$ Ref. 43

Where K = Equilibrium constant,
[D] = Donor concentration,
Δ^A_{AD} = Difference between the chemical shift of the complex and that of the acceptor.
K = Intercept/Slope = 0.11 l $mole^{-1}$
Correlation Coefficient:0.999

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BIOGRAPHICAL SKETCH

K.N. Sivaramakrishnan was born in Madras, India. After an uneventful schooling, he received Bachelor's and Master's degrees in Chemistry at the University of Madras. In September, 1971, he joined the Graduate School at the University of Florida. After graduation, he plans to spend more time on research in chemistry and on his hobbies which include astronomy, music, sports, and philosophy. Someday he also hopes to be a "Renaissance man" in the true sense of the word.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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